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PCBS INVOLVEMENT IN THE
PULP AND PAPER INDUSTRY

Task 4

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ABSTRACT

The sources, distribution, and losses of PCBs in the U.S. pulp and paper industry are discussed in detail. The major source of PCBs to the industry is recycled carbonless copy paper manufactured from 1957 to 1971, but the amounts of PCBs from this source diminished rapidly after 1971. A model showing past and projected PCBs content in product and wastewaters from the industry is presented and discussed. Estimated costs (worst-case basis) for wastewater treatment to achieve one ppb PCBs in effluents from the industry are developed; results indicate a 3 to 5 percent product cost increase will result from such treatment.

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APPENDIX I

INDUSTRY INTERVIEWS AND PLANT TRIPS

I-1.0 OBJECTIVES OF INDUSTRY INTERVIEWS AND DISCUSSIONS

From previous efforts under Task I of Contract 68-01-3259, it was apparent that the data available concerning PCBs in the paper industry were sparse at best, and that extensive efforts would be required to gather sufficient information for the model development and interpretation. The gathering of such information was the major objective of all industry contacts during this work; early in the program industry was made aware of the purpose of and our approach to the work. Subsequent response and cooperation by the industry were uniformly excellent.

Specific areas covered during the interviews and discussions included:

- 1) The level of awareness of the PCB problem within the industry;
- 2) Analytical data (on PCB levels in products and effluents) which might be available or which might be obtained and made available at a later date;
- 3) The possibilities and practicalities which bear on treatment of mill effluents, or on internal water reuse and purification systems;
- 4) Present trends in treatment technology as the mills prepare for adherence to the 1977 and 1983 effluent quality criteria;
- 5) The standard practices of sampling and analysis which generate the data base of PCB levels in the plants;
- 6) The similarities and differences found between production mills operating under current bounds of raw material, energy, labor and treatment costs; and
- 7) PCBs transport within the plants.

I-2.0 MEETINGS WITH TRADE ASSOCIATIONS

I-2.1 Meeting with API

In mid-July, 1976, a meeting was held in Washington, D. C. with representatives of the American Paper Institute (API), the Boxboard Research and Development Association (BRDA), the National Council of the Paper Industry for Air and Stream Improvement (NCASI), senior staff members from several API member companies, and the EPA Office of Solid Waste Management Programs (OSWMP). The approach to the program, and particularly the PCBs-industry model, was outlined and discussed in detail. Cooperation and needed information were solicited, and plans for the provision of available or anticipated data were made. All areas noted under Section I-1.0 were covered.

I-2.2 Meeting with Institute of Paper Chemistry (IPC)

On August 6, 1976 a meeting was held with staff members of the IPC in Appleton, Wisconsin. John C. Wollwage, Vice President-Research; Dr. H. S. Dugal, Director, Industrial and Environmental Systems Division; Dwight B. Easty, Group Leader, Analytical Chemistry, Division of Natural Materials and Systems; Mr. George Dubey; and Mr. Peter Parker (all of IPC) took part in the discussions.

At that time the IPC was performing an in-house study aimed at development of an improved procedure for PCB analysis in pulp and paper mill matrices. They had attacked the question of PCB partitioning in mill flows and found PCBs to be substantive to fiber, associating most notably with the small particulate constituents (fines) of the pulp/water system. White water high in fines content is routinely recycled in order that as much of the fiber as possible eventually become products since fines have a desirable effect on the qualities of opacity and surface smoothness. Economical use of the raw fiber requires a minimization of the fines loss. Such a procedure appears to preferentially associate the major portion of any PCBs with the paper product.

It was also agreed that the PCB concentration in the waste sludge might reasonably be assumed to be at the same concentration as in the product.

In other words, if the PCB levels in paper product is in the low parts per million range, PCB levels in the sludge will also be in this range. The limited sludge data obtained supports this contention, and at the same time shows paper mill sludges to be comparable to municipal treatment plant sludges in PCB content (ranging up to 23 ppm) (14).

The majority of PCBs introduced to papermaking as part of the wastepaper input were believed by the IPC personnel to be still enclosed in the gelatin-gum arabic microballoons. The microballoons (10 - 20 microns in diameter) are known to be substantive to fiber. They release their PCB load for analysis upon treatment with alcoholic KOH solution. It was not known what fraction of the incoming capsules may break open, nor whether the pulping and refining steps may cause breakage, but it was suspected that relatively few of the microballoons would rupture during the papermaking process.

In addition, it was decided that PCBs in intact capsules would not participate in evaporation as "free" or "wild" PCBs may be able to do. Mass balances done by IPC on some paper mills have given an indication of a possibility of evaporative losses, but not in large amounts, nor in amounts which would jeopardize the overall conclusions or credibility of the model presented in Section 5.0 of this report.

During the analytical methodology work by IPC, small amounts of PCB used to spike solutions showed significant evaporative losses. This has resulted in a strong recommendation for the minimization of sample transfers and handling in analysis for PCBs.

Present analytical capabilities at IPC show detection limits for paper to be 0.1 ppm PCB and for solutions to be 0.1 ppb PCB. Both call for a trained operator conversant with and practiced in routine PCB analysis.

Interferences on the chromatogram appear to be removed in good part by oxidation of the sample with chromium trioxide. These interferences seemed to be peculiar to the types of matrices found in pulp and paper processes. Attempts to simplify PCB analysis by perchlorination of all PCBs to decachlorobiphenyl were found to give unsuitable results. This treatment

appeared to have converted some non-PCB components of carbonless copy paper into a form which could be incorrectly identified as PCBs.

Other aspects of the problem and of the IPC program were discussed in detail. Many of these are discussed or referenced elsewhere in this report. The results of this meeting served to solidify the approach to the model and the selection of parametric values to be used in exercising the model.

I-3.0 PLANT VISITS

Seven paper mills were visited during the program; four of these utilized between 50 and 100 percent recycled material. The others either were companies known to be very much aware of the PCBs problem and using some recycled fiber or mills using only virgin fiber. Short summaries of the trip reports for these plants are included below. As will be noted, some plants are not named in these summaries.

I-3.1 Plant A - 100 Percent Recycled Raw Material

General Description

Plant A employs approximately 300 people and has a Fourdrinier, two cylinder machines and a Printer Tinter. The raw material used is wastepaper which has been sorted, graded, baled and marked by organized paper stock dealers throughout the Midwest. The most important grades used are reclaimed corrugated containers, mixed paper, newspaper and clippings trimmed from box shops and converting plants. Much of the stock is picked up in large cities by company trucks as return loads after delivery of the finished board. This re-use of secondary fibre eliminates a large amount of paper tonnage being sent to landfill or incinerated. In 1971 85,000 tons of wastepaper were reclaimed through this plant.

The basic product manufactured from the wastepaper is paperboard. This product is used for core stock, tube stock, wrapper, carton, paper box, book bindings, and globe stock.

Pulping, Cleaning and Refining

The first step in converting paper stock to pulp is called hydration; machines called hydropulpers are used. These are large tubs with a rotating disc in which the dry paper is mixed with warm or hot water. Chemicals may be added to aid in the dissolving process and to destroy any bacteria which may be present. Most of these machines operate on a continuous process. As soon as the fibers are dissolved fine enough to be extracted through 1/8" holes they are screened off.

The various cleaning and refining processes which follow pulping are typically a spin-off to remove light particles of foreign material, and settling to remove heavy dirt. In addition, there are several systems of mechanical screening to remove coarse or undefibered bundles and dirt. Not the least important is a treatment of high pressure - high temperature steam followed by a refining process for the purpose of breaking down foreign materials like pitch, wax, or asphalt which may be found in the wastepaper.

After the paper stock is cleaned and defibered, it is stored as a liquid suspension in large chests. Before going to the paper machine the stock is again refined or "brushed out" in machines called Jordans or Refiners, mixed to an exacting consistency with water and screened one last time.

Papermaking

Plant A employs both Fourdriner and cylinder-type paper machines. The latter employ cylinders covered with fine mesh wire to extract pulp from the slurry stock onto the surface. The material is then deposited in thin layers (one from each cylinder) to form the wet web. After all the cylinders have deposited their contribution of fibers, the wet web of paper is pressed to remove excessive water. Each pair of press rolls gradually increases the pressure until the wet web is dry enough and strong enough to support its own weight when it leaves the press section.

The Fourdrinier machine employs a long wire belt for formation of the wet web. Paper stock is fed onto the moving wire through a sluice from

a headbox, and, in contrast with a cylinder machine, the web is made up as a contiguous single layer. Over a relatively short distance enough water drains through the wire by gravity and by passing over suction boxes that the mat can leave the wire and pass onto a felt where pressing begins.

All machines employ a long section of many steam heated cylindrical dryers. As the sheet leaves the wet end after all possible moisture has been removed by mechanical pressing, the remaining excess moisture must be removed by evaporation. The sheet of paper passes over all of these dryers which eventually produces a dry sheet to customer specifications.

The last step in the actual paper manufacturing is calendering or pressing for the purpose of obtaining a uniform finish and thickness. Also at this station it is possible to apply surface sizing or other forms of coating or stain.

After passing through the calenders the paper is wound onto reels to be rewound and trimmed to meet size orders. If the customer wants his paper in flat sheets, it is run directly from the paper machine through a sheeter. In either case, when the paper is finished it is banded, wrapped, labeled, and weighed.

A substantial amount of the total production of Plant A is sent to a converting plant for further processing. Most of this processing consists of slitting wide rolls into narrow widths to be used for winding into cores and tubes. This plant also performs cutting from rolls into sheets, precision trimming of sheets, and laminating.

I-3.2 Plant B - 90 Percent Recycled Raw Material

General Description

This plant is a major manufacturer of tissue items, producing 800 tons of facial tissue, toilet paper, napkins and paper towels per day. Approximately 90 percent of the raw material required is supplied by waste paper, which is a slightly higher percentage than most other tissue mills.

Plant personnel supplied a report on PCBs generated by them in 1975. The concern for effluent water quality dates back to the establishment of a primary treatment system in conjunction with the start-up of a deinking process in the 1930's. The secondary treatment system was put into operation several years ago, prior to the regulations governing suspended solids. A tertiary process is in the development stage at the present time. PCB measurements were begun in-house during 1975. Data on PCBs content of products prior to 1975 have been obtained and are reported elsewhere.

Characterization of Raw Material

Although most of the raw material for this plant is wastepaper, less than 50 percent of this is classed as post-consumer waste; in other words, most of the returning paper stock has never been previously recycled. Office wastepapers of the ledger grades are removed from the incoming stock, but a quantitative screening of all returning paper stock is impossible from an economic standpoint. As shown by industry data and the modeling effort in this report, even a few sheets of the carbonless copy paper can have an observable affect on PCB concentrations in a single day's output.

Office wastes in general do not make a desirable paper stock, since many office paper products contain binders, colorants or other minerals that are difficult to remove and cause problems in the papermaking process. These wastes are purchased by the mill primarily to assist their paper dealers. They do become more important during periods of short paper stock supply.

Effluent PCB Levels

PCB concentrations in clarified mill intake water were less than 0.1 ppb. Measurements of deinking, mill and combined effluents were reported to range from 0.3 to 2.7 ppb.

In-Plant Vaporization Estimate

The plant has performed a water mass balance on its paper machines. An average of 570 gal. per ton of product was lost. Assuming the production of 800 tons per day and a water concentration of PCBs (excluding

PCBs bound to fines and assumed not to evaporate) of 0.1 ppb, evaporative losses would be 0.00038 pounds of PCB per day or less than 0.15 lbs/year. This is probably an undetectable loss if direct measurement was attempted.

I-3.3 Plant C - 80 Percent Recycled Raw Material

Pulp Generation

Pulping is a batch process at this plant. Wastepaper, accounting for about 80 percent of the raw material, is added to pulpers #3 and #4 together with hot water and caustic soda. Steam jets raise the temperature to about 185°F and deinking continues for about 1.5 hours. After deinking, the stock from both pulpers are dumped together yielding a stock slurry of about 7 percent consistency. From here the stock is passed through a one inch bar screen that removes large contaminants such as string and rags. The pulp is now pumped to a holding chest.

Manually operated valves determine the quantity of stock discharged from the holding chests through two 1/8-inch screens. The accepts here have a concentration of about 4.5 percent, and rejects from the screens are trucked to a landfill. Accepts are stored in another holding tank.

Upon leaving this tank, the stock is diluted to about 0.7 percent solids and run through centrifugal cleaning to remove fine contaminants. Accepted stock is now directed to a screen with 0.010 inch slots. Accepted stock from this screen pumped to two slope washers that have counter-stock flow of water. These washers are arranged in series with the second one increasing the stock consistency (solids concentration) to about 5 percent.

At this point the stock is pumped to two washers set up in parallel. The washed stock, with a consistency of about 2 percent solids, is pumped to a storage tank until the chlorination tank is ready for a new batch. Water for the washers comes from the slope washers.

During chlorination, chlorine gas is pumped into a tank holding the stock and allowed approximately five minutes retention to react. The stock batch is then pumped towards a vacuum washer. However, before it is washed, sodium hydroxide is added which reacts with any residual chlorine to form

sodium hypochlorite to augment the bleaching process; the final pH is 9. The bleached stock is sent to retention tanks.

The stock pulp is sent to a vacuum washer to remove materials made soluble by chlorination. This wash water originates from the paper machine water supply, the white water. The filtrate from the washing process is pumped to the slope washers which conditions the new batch for chlorination by reclaiming the chemicals and also reduces the amount of water used. The stock pulp now has a consistency of about 5.5 percent. Upon leaving the washers, the stock pulp is pumped to high density storage tanks to await the papermaking operation.

This mill also has a separate pulping system for virgin pulp and pulp substitute. However, both virgin and substitute pulp are blended with the wastepaper stock pulp. Here, chemicals are added to develop better fiber bonding strength.

Papermaking

From the storage tanks the stock pulp is diluted to about a 0.3 percent consistency and pumped to the headbox. Prior to entering the headbox, the pulp is rewashed, rescreened and run through a three stage centrifugal cleaning system. Much of the water used in papermaking is recycled. Excess white water is stored to be utilized in various operations in the mill.

The sheet is pulled through on a felt belt and dried. The speed that it is pulled through regulates the strength of the product. Thickness is governed by this speed and by slicing the sheet off the belt with a doctor blade. Several plies are then rolled together to produce a paper of desired specifications.

Water Source and Effluent Treatment

Plant C uses municipal water which is believed to be relatively low in PCBs. The intake volume is about 1.5 million gallons per day.

The discharges from Plant C enter a wet well from which the wastewater is screened and sent to a company-operated treatment plant.

Treatment consists of primary clarification and a two-stage activated sludge system. The treatment plant effluent is discharged to the Fox River (mid-stream).

I-3.4 Plant D - 50 Percent Recycled Raw Material

Plant D is a major recycling operation. Six grades of wastepaper (e.g., office and foodboard) are the major constituents of the raw materials utilized to produce acceptable deinked pulp stock. This accounts for approximately 50 percent of the required pulp with the remaining being composed of purchased virgin pulp and pulp substitute. There are essentially two pulping systems - one for wastepaper and deinking and the other for the virgin and substitute pulp.

Pulping and Fiber Recovery

Here, wastepaper is mechanically broken down with hot water (about 190°F), caustic soda, surfactants and deinking chemicals by means of a ribbed rotor at the bottom of the hydropulper. Much of the heavy waste such as metallic objects and plastic sheets are collected in traps at the bottom of the pulper. At this point, the pulp stock has about a 6 percent consistency (consistency being the percent solids to liquid).

The deinked pulp leaves the hydropulper through perforated plates and is pumped to blending chests for additional retention time and agitation. The pulp now has about a 2.5 percent consistency. Upon leaving the chests, the pulp is passed over a filter that recovers the cooking liquor in the filtrate. The filtrate is reused in the pulper to recover the heat and residual chemicals. Excess washer water is reused for other operation dilutions. Water is extensively recycled in the deinking operation.

The pulp is now sent to centrifflers, which are centrifugal cleaning devices for removal of pins, staples, and other heavy particles. The accepted pulp has a 2 percent consistency and it is sent to a centrisorter pressure screen. Accepted stock from the pressure screen goes on to washing while rejects are passed through a deflaker and then across a screen for further fiber recovery.

The pulp then enters a four-stage counter-flow washing system. The first stage consists of 2 cylinder washers, the second and third stages consist of sidehill washers, and the fourth is another cylinder washer. The cleanest water is used for dilution at the fourth stage and the filtrate is fed to the preceeding (third) stage. This filtrate is then used in the second stage and its filtrate in the first stage, where the filtrate is discharged to waste treatment. The water in the washing process originates from the discharge of the paper machine water, white water, and the acid and alkaline bleaching water.

Following washing, the stock is bleached with chlorine, followed by treatment with caustic and then hypochlorite. The next treatment is a three-stage pressure screen system. Accepted stock pulp from the first stage pressure screen then goes to a five-stage centrifugal cleaner system for removal of small heavy contaminants such as ink. Those fibers rejected are replaced in the centrifugation scheme to concentrate the contaminants and unacceptable pulp, and to reclaim as much of the shunted acceptable pulp as possible. Following this is a four-stage system of centrifugal reverse cleaners for removal of lightweight contaminants such as plastic fibers and adhesives. After the cleaning system the stock goes to the final washer for thickening and storage in high-density towers. The water removed by the thickening process is reused in other washings and in the bleachery.

The above description for secondary pulp supplies 50 percent of the materials required to meet the current demand of Plant D. The remainder is composed of purchased virgin pulp and pulp substitute. Both are warehoused in solid form and repulped in their respective hydropulper, using recycled paper machine white water. This pulp is then pumped to storage chests until needed. From here, the pulp is sent to refiners for fiber shortening and fibrillation to enhance greater bonding capacity.

From the refiners the pulp is discharged into a pipeline that contains the secondary pulp for blending of the types. After sufficient time to ensure homogeneity, components such as clay, titanium dioxide and alum, to name a few, are added to the stock pulp as it moves to the paper machine.

Papermaking

Stock taken from the high density storage tanks is diluted and pumped to the papermaking system. Here the stock volume is controlled to insure a constant head level. By operating under a known head, the texture of the pulp sheet falling on the Fourdrinier remains the same throughout the operation.

The endless mesh belt of the Fourdrinier effectively drains enough water from the pulp slurry to permit the fibers to make a sheet called the wet web. Much water is recycled during papermaking operations. Since this water is falling from the bleached product, the pulp imparts a white color on the water and hence is called white water. Because water is continually being added here, there is an excess overflow. This surplus water is stored and used to supplement the water diluting the deinked stock. Several hundred thousand gallons of water escape each day due to evaporation while the paper is being pressed and dried. When the pulp leaves the headbox, it is 99 percent water; after passing through the presses, it is about 60 percent water, and after the driers, only about 5 percent moisture remains. This is the percent moisture of the rolled product.

Intake Water and Wastewater Treatment

Since the product color and composition is highly important, the water used throughout the operations necessarily should not contain any suspended contaminants that are able to be removed. Therefore, this mill has a treatment facility for intake water, utilizing flocculation with alum and lime, addition of algacide, and filtration. The filter is composed of the following: top layer - 8 inches of coal; middle layer - 2 feet of sand; bottom layer - 2 feet of crushed stone.

Currently, this mill only has primary treatment, a clarifier. The present system has about 90 percent SS removal but only about 25-30 percent O&D reduction. The effluent from this clarifier is being discharged to the Fox River. The average flow for 1975 was 3.9 MGD. This volume can be broken down as follows:

- 2.5 MGD from deinking
- .9 MGD from papermaking
- .3 MGD from water plant
- .2 MGD disposal plant and misc.

Under construction now at Plant D is a 2-stage activated sludge system. Preliminary investigations on this type of treatment facility for pulp and paper wastewater discharges indicates that this system is very effective at further reducing the SS levels and greatly reducing effluent BOD.

Clarifier sludge contains 10 percent solids and is further consolidated in compaction tanks to a 12 percent solids level. The sludge is further dewatered to 28 percent solids by lime addition and subsequent vacuum filtering. The filtrate is returned to the primary clarifier and the dewatered sludge is trucked to their private landfill.

Landfill Operations

The company has opened a new landfill which covers about 18 acres. Preliminary geologic investigations revealed a solid bedrock foundation. The area is encompassed by a man-made compacted clay dike, effectively eliminating any surface runoff from the landfill.

Concern for groundwater contamination resulted in the construction of monitoring wells. There appears to be two layers of groundwater separated by a clay table. When completely filled, the landfill will be slightly dome shaped with a 2 degree slope.

I-3.5 Plant E - Less Than 50 Percent Recycled Raw Material

General Description

Plant E is basically self-contained, i.e., it produces in-house nearly 50 percent of their fiber requirement by chemi-mechanical treatment on hardwoods. The remaining 50 percent is composed of purchased bleached kraft pulp from Canada and other U. S. sites and such items as foodboard, cups, and IBM cards. No carbonless paper is utilized. Production is between 300 and 400 tons per day.

Product PCB levels from Plant E have consistently remained below 5 ppm proscribed by FDA. Effluent levels of PCBs are also apparently lower than most of the industry using reclaimed fiber, probably because of efficient removal of suspended solids in the waste treatment systems.

Pulping

Plant E uses chemi-mechanical pulping, virgin pulp from purchased bleached kraft-pulp, and secondary pulp from wastepaper. Each operation occurs in a specific pulper and the stock is blended later according to product specifications. The virgin pulp slurry is generated by only adding hot water while the secondary pulp requires hot water plus caustic soda plus hypochlorite bleaching powder. Both virgin and secondary stock pulp are not stored but directly mixed with the chemi-mechanical pulp stream. Plant E is a continuous operation, and all grades of pulp are being used simultaneously but only that from the chemi-mechanical system is allowed a detention.

Blending of pulp grades occurs in machine chests, each having a different percentage of the grades depending on the eventual product. It is just prior to these chests that other additives such as clay and other fillers are added to provide the required paper characteristics.

Papermaking

Each pulp stream is passed through similar machines, with all machines having an additional coating step. The stock pulp enters the Fourdriner to produce the wet web, approximately 19 percent of the water content is voided here (in other words the web's consistency increases from 0.5 to about 20 percent). The wet web is then drawn through a series of presses to further remove the water. The majority of the remaining moisture is removed by drawing the sheet through a series of dryers. Final moisture is about four percent.

Following the drying operation, the sheet is passed through rollers to smooth it and produce a uniform thickness. It is then rolled, trimmed, cut and warehoused. Some cut rolls are sent directly to a specification cutting section for high-demand dimension consumer products (a sizeable fraction of the total production is used for telephone books).

Waste Treatment

This plant utilizes two waste facilities; a fluidized bed incineration for spent liquor in the pulp mill operation, and a wastewater treatment plant for water used in the papermaking process plus excess wash water and associated solids from the pulp mill.

The chemi-mechanical pulp mill effluent with a 6 percent solids content is sent to an evaporator where the solids content is increased to about 45 percent. The liquor, now a syrup, is placed in the incinerator operating at approximately 1300°F, and the remaining moisture is flashed off allowing the organics to be volatilized. At the bottom of the unit, air jets keep the ash in motion (fluidized). Therefore, pulp mill activity is a closed system with no effluent, and the excess ash is trucked to a landfill.

Wastewater currently receives only primary treatment in two parallel clarifiers, but removal of approximately 96 - 98 percent of the suspended solids is achieved with 40 - 50 percent BOD removal. A new secondary treatment system will begin operations in the near future. Overflows from the clarifiers will be combined and discharged to the secondary treatment reactor, which is a closed, oxygenated, three-segment tank. Effluent from the reactor is then sent to a settling tank and after a determined retention time the supernatant liquid is discharged to the Fox River. The new system is designed to handle 6.5 mgd with a three hour retention. The mill has recently reduced its water requirement from 8 mgd to 6.8 mgd in preparation for the secondary system.

The sludge will be removed with some of it reused as seed in the oxygenated reactor tank while most of it will be dewatered to about 22 percent solids by a vacuum filter. This waste sludge is presently deposited on a landfill. There is no monitoring for groundwater contamination at this time.

Management is currently communicating with other mills that may be able to use their sludge as it contains a high fiber concentration that can be used for other paper products.

I-3.6 Crown Zellerbach Research Laboratory and Camas Mill

A meeting with Dr. Herman R. Amberg, Director of Environmental Services for Crown Zellerbach and members of his staff was held on June 29, 1976, at the Central Research Division in Camas, Washington. Crown Zellerbach has a number of mills which range from total use of virgin fiber to complete dependence on secondary fiber. Since most chemical analyses are done at the Central Research location, it was felt that the question of analytical accuracy could be de-emphasized and relative differences in PCB concentrations assessed.

CZ analytical detection limits for PCBs in paper were routinely 1 ppm and are apparently dropping under continued attention to details of the analysis. Some data had been taken as far back as 1971. A number of important points were discussed:

- 1) No measurable PCBs had been found in virgin wood.
- 2) Exhaustive sampling and analysis had failed to identify any PCB generation during the pulp bleaching stages.
- 3) Process chemicals were surveyed to identify any sources of PCB and none were found.
- 4) Data would be made available through API.

A tour of the Camas Mill, which makes specialty papers, was taken. This mill used virgin pulp, a small amount of purchased pulp, sawdust and wood chips from surrounding sawmills as its raw material. Inputs of PCB were therefore limited to that occurring in the intake water.

I-3.7 Weyerhaeuser Company

On June 25, 1976, Dave Morris and Ted Ross of the Weyerhaeuser Corporate Engineering Department at Tacoma, Washington met with a Versar representative. Mr. Ross had previously been involved with EPA contract work which related to effluent guidelines for the pulp and paper industry and both were following PCB-related matters.

Weyerhaeuser's papermaking operations are based on a 100 percent virgin fiber raw material. As a result, it was believed that this mill would only encounter PCBs that were associated with the intake water, or as a result of internal PCB uses in transformers or capacitors. Contingency spill plans were set up in every mill; transformers containing PCBs were diked and monitored for any signs of leakage.

1.0 EXECUTIVE SUMMARY

1.1 Historical Background

In 1966, Soren Jensen reported the presence of PCBs (polychlorinated biphenyls) in Swedish fish and wildlife as a result of a study begun in 1964. The Food and Drug Administration began, in 1967, a program to develop analytical techniques for PCBs. During this period concern about PCBs in food and in the environment of the United States was increasing. In 1969, FDA alerted its Districts to expect PCBs in food samples, and to analyze for PCBs in foods sampled for pesticide analysis. Findings of PCBs in fish, milk, eggs, and poultry samples occurred throughout 1969 and 1970.

In August, 1971, a significant level of PCBs was found in a grain and cereal composite of a Market Basket sample by FDA in their Total Diet Studies, and the contamination was traced to the greyboard packaging of a cereal. According to FDA (supporting data for Press Briefing by Dr. C. C. Edwards, September 29, 1971), the highest PCBs level found in greyboard was 433 ppm. FDA met separately with the American Paper Institute and with food manufacturers in September, 1971 to inform them of the PCBs problem in foodboard and to discuss approaches to its solution.

By the end of September, 1971, all concerned parties appear to have agreed that the major source of greyboard contamination was recycled carbonless copy paper which was known to contain PCBs. Production of this material had ceased as of June 1, 1971, but recycling was continuing. In the same time frame, Monsanto Industrial Chemicals Co., essentially the sole U.S. producer of PCBs, announced cessation of sales for all but closed electrical systems (capacitors and transformers) applications.

On July 6, 1973, the FDA issued its final rule-making document on tolerance levels of PCBs in various foods and paper food-packaging material (10 ppm for paper food-packaging). By this time the paper industry had succeeded in reducing PCB levels in food-packaging materials made wholly or partially from recycled fiber to well below the FDA tolerance limit. This appears to have been accomplished through more judicious selection of recycled fiber for foodboard manufacture, including:

- (1) Cessation of use of cutting scrap from office form production (where carbonless copy paper content could be very high); and
- (2) Limitation or selectivity in the use of office waste for foodboard production.

Levels of PCBs in foodboard have generally continued to decline since 1973 to a current level of less than one ppm, except for occasional "hot spots" resulting in levels of up to five ppm. These "hot spots" are generally attributed to the inclusion of significant quantities of outdated office files containing carbonless copy paper. PCB levels in other paper products are also in the one ppm or below range; those made from virgin pulp, of course, exhibit by far the lowest PCB levels.

1.2 Carbonless Copy Paper

Aroclor 1242, a mixture of PCBs containing an average of 42 per cent chlorine, was purchased from Monsanto and used in carbonless copy paper as an ink carrier or solvent during the period 1957-1971. The total amount used for this purpose was 44,162,000 pounds, approximately 28 per cent of the total estimated Monsanto sales for plasticizer applications and 6.3 per cent of Monsanto domestic sales of PCBs during 1957-1971. The average content of Aroclor 1242 in the carbonless copy paper was 3.4 per cent.

The National Cash Register Company (NCR) was the developer and sole marketer of the PCB-containing carbonless paper, although Appleton Coated Paper Co., Appleton, Wisconsin; Mead Corp., Dayton, Ohio; Combined Paper Mills, Combined Locks, Wisconsin; and Nekoosa-Edwards Paper Co., Port Edwards, Wisconsin, at one time or other performed the actual production under license from NCR.

The Aroclor 1242 was used as a solvent for certain color reactants which were encapsulated into microspheres producing aggregates 10-20 microns in diameter and applied to one side of the paper during the coating process. The walls of the microspheres were an aldehyde-hardened gelatin-gum arabic formulation which ruptured and released the dye under application of local high pressures as from pens or pencils. In 1971 alkyl-biphenyls were used as the dye carrier in place of Aroclor 1242.

It should be noted here that PCBs, primarily Aroclor 1254, were used to a limited extent in printing inks. The total usage in this application is estimated at 50,000 pounds, primarily in the 1968-71 time frame. No other actual or potential usage of PCBs in paper product or usage besides the copy paper and these inks has been definitely identified to date.

1.3 PCBs in Paper Mill Effluents

It has been recognized for several years that effluents from paper mills contain environmentally significant quantities of PCBs. The PCBs in these wastewater streams are generally more similar to Aroclor 1242 than to any of the other Aroclors or to PCBs found in the general environment and biota (which tend to exhibit chromatographic fingerprints corresponding to higher chlorine contents than 1242). Thus, although introduction of PCBs into paper-making processes through process water usage undoubtedly occurs (PCB levels at water intakes of paper mills average about 0.1 ppb), the major source of process contamination by PCBs appears to be carbonless copy paper contained in recycled wastepaper.

A number of paper mills, in response to the need for improvement of water quality, have installed or are now installing waste treatment processes which are expected to greatly reduce the PCB levels in their effluents. However, these levels may still be typically above the one ppb level proposed by EPA on July 23, 1976 as an effluent standard for capacitor and transformer manufacturers, and the quantities of wastewater from paper mills are generally much larger than from such equipment manufacture. In addition, sludges or concentrates from paper mill water treatment may be sufficiently high in PCBs as to warrant concern about proper disposal.

The magnitude of the PCB control problem is illustrated by the existence of 230 paper mills producing pulp completely derived from recycled wastepaper and 550 other facilities utilizing some fraction of secondary fiber in their pulp production (typically 10 to 15 per cent). Recycled wastepaper amounts to about 13 million tons per year as a pulp source, third in importance to pulpwood and forest product wastes.

1.4 Purpose and Objective of the Reported Work

The purpose of the work reported herein was to bring together all relevant information and data concerning PCBs in the paper industry, and to interpret these data with regard to present and future environmental significance. Specifically, the report addresses the sources, transport and release of PCBs throughout the paper industry; the historical perspective and projected future impact of PCBs usage in carbonless copy paper; and a preliminary account of technology and costs associated with abatement of PCBs in paper mill effluents. The data obtained on intake and effluent PCB levels, on paper recycling statistics, etc., from industry and other sources are also discussed.

There appears to be general agreement that the entry of PCBs into the paper industry was completely unintentional, that the industry responded well to the need for reduction of PCB levels in food packaging, and that waste treatment systems for suspended solids removal (albeit installed for purposes other than PCB control) will significantly reduce PCB discharges from the industry. Nevertheless, continuing and increasing concern by the public and by state and federal agencies regarding environmental and human health effects of PCBs, including contamination of food packaging materials as well as PCBs in wastewater, have repeatedly focused attention on the paper industry, much to the concern of that industry. The objective of this report is to present the actual situation, as accurately as possible, in order to serve those who must make regulatory decisions potentially affecting a valuable resources recovery industry.

The concern of the industry was reflected in their excellent cooperation with the project. Cooperation and support from federal and state agency personnel were also uniformly excellent. However, it should be noted that, in general, there was a scarcity of data in several relevant areas, particularly historical data prior to 1975; this was the major limitation to the accuracy and completeness of the results obtained. Results of industry visits are presented in Appendix I.

1.5 Major Results of the Study

Since 1971, when NCR carbonless copy paper was no longer manufactured with a PCB dye solvent, PCB concentrations in paper products, effluents and sludges

have shown a precipitous decline. The former are now in the 0-1 ppm range for most products tested. Effluents have dropped as the result of better suspended solids removal in compliance with BPCTCA and approaching BATEA requirements. Sludges seem to have approached the range of <1 to 24 ppm PCB common for municipal treatment plants. The driving force has been the reduction in NCR carbonless forms being recycled, and the final disposal by incineration or landfilling of a large annual fraction of the paper industry's output. The present 19% recycling rate shows that 81% of the annual production is not available to be recycled and carries its PCB load to the landfill or the atmosphere (via incineration of wastes).

A search for evidence of "pulses" of PCB as old files are recycled failed except on a one-mill/one-day basis. The 40 million pounds of PCB put into the carbonless copy paper has been routed through the wastepaper stream each time losing 80% of the previous year's mass, and being further diluted by virgin wood pulp and forest product residue pulps. As of 1976 the average product concentration as well as influent and effluent levels had all fallen to the point where the sensitivity and detection limits of the analytical methods for measurement required improvement. The FDA reported⁽⁷⁾ a decrease from 15.3 ppm in recycled (food packaging) paperboard in 1972 to 1.4 ppm in the same material in 1974.

As the introduction of PCB has decreased in the recycled waste paper stream, the fraction of product PCB arising from the input water has increased, but this contribution does not appear to be significant at present. For a 0.1 ppb intake water concentration, total removal to the pulp will produce (in a paper requiring 13,000 gallons per ton) a PCBs concentration of 0.005 ppm. As an example of just how directly the effect of the carbonless copy paper acts, the same concentration (0.005 ppm) would result from the PCBs found in 0.14g of copy paper ... less than one 8 x 10 inch piece.

The historical perspective shown by our mathematical model, and validated by the available data, show PCBs in paper mill effluents and product to have passed a maximum in the 1970-1971 period and to be continuing down to pre-1957 levels under the influence of declining amounts of PCBs in the recycled waste paper stream and the low effective concentrations found for intake waters.

On-site measurements and laboratory experiments have shown the PCB to be substantive to fiber; that is, preferentially associated with the fibers rather than the water in which they are carried. Highest PCB concentrations in fiber slurries are associated with the smallest fiber particles, the "fines". Economical utilization of the fiber requires it to be exhaustively recycled in attempts to associate it with the paper being manufactured. Fines control porosity, surface finish and affect brightness of the product. Discharge of PCB from a typical mill thus appears to be primarily by way of the suspended solids. Removal of suspended solids accomplishes PCB removal, and a consideration of the high surface to volume ratio of the smaller particles shows why they are the ones that need to be removed for a low PCB effluent.

A continued trend of increased water recycling is exhibited by the industry, for the purpose of minimizing external treatment costs as well as recovering chemicals, heat and raw material from process streams. This has culminated in the design and construction of a totally process-effluent free bleached kraft pulping mill in Canada. Only non-contact cooling water will be discharged. New end-of-pipe treatment systems, such as the Zurn-Attisholz 2-stage activated sludge system installed by Wisconsin Tissue Mills, offer promise of significant reductions in BOD and suspended solids/PCBs. Cost estimates for carbon absorption treatment (end-of-pipe) range from \$886 to \$1227 per pound of PCB removed.

Some data exists to show net removal of PCB from an intake water as evidenced by a lower concentration in the effluent. The paper-making process in such a case is withdrawing the PCBs from the environment and stabilizing them in the much less mobile paper phase. Of course, numerous routes whereby these PCBs can become remobilized (in air or water) are available.

It is believed that essentially all of the Aroclor 1242 used in carbonless copy paper has been released to the environment (assuming negligible degradation). At the present time more than half can be attributed to landfills and the remainder dissipated. In a sense, these PCBs were mobilized upon the initial production of the paper, and their passage through paper mills merely resulted in partition between the accepting media (water, air, solid wastes, products).

2.0 PROCESS TECHNOLOGY OF THE PULP AND PAPER INDUSTRY

2.1 Background

Pulp and paper manufacturing consists of two distinct processes. Pulping is the reduction of whole wood or waste paper into a semi-liquid fibrous mass, while papermaking consists of forming discrete fibers into paper sheet or paperboard. There can also be ancillary operations which provide special features such as coloring, coating and backing.

The processes require four basic raw materials: fiber, water, energy and chemicals. In contrast to the earliest mills, newer mills may be located some distance from their fiber source, especially in the case of recycling-oriented mills where proximity to fiber means an urban center rather than a forest. The water requirement is definitely being reduced in magnitude as recycling methods are being developed within the industry. The recycling has the benefit of assisting in meeting more stringent discharge criteria as well as recovering chemicals from process waters and meeting energy needs by recovering energy from organic wastes.

The wood used in pulp and paper manufacturing is called pulpwood. It can be either hardwood from deciduous broad leaf trees, or softwood from coniferous or needlebearing trees. This categorization reflects the proportion of cellulose to lignin (the substance which holds the fibers together). The supply arrives at the pulping facility as logs, chips made from roundwood, as sawdust, slab or chip residues from saw mills.

In traditional logging practice, the central portion of the tree was utilized in the pulping mill requiring a removal of the bark from the log. Mechanical debarking or hydraulic means are used with the bark often collected and burned as an energy source.

2.2 General Pulping Techniques

Regardless of the type of process involved, the basic objective of pulping is to reduce the wood to non-woody fibrous materials by rupturing the bonds between the fibers of wood. This task entails either cooking the pulpwood (using suitable chemicals) in a digester under controlled conditions of

time, temperature, and pressure or reducing the wood to fibers by mechanical or semichemical means.

2.2.1 Mechanical Pulping

Mechanical pulping, sometimes called "the groundwood process," operates by mechanical means, generally using either a large grindstone or a machine called a "refiner". The present methods of manufacture do not differ in principle from that of 1867, though the size, capacity and form of the grinders have undergone much change. In all equipment the logs of wood are pressed against the face of a rapidly revolving grindstone in such a way that the length of the log is parallel to the shaft holding the stone. In the older grinders, logs two feet long were placed by hand in pockets attached to the grinder frame, and were forced against the stone by pressure plates operated hydraulically. Usually there were three pockets on each stone so that one could be opened, filled with wood, and put back into operation without shutting down the entire grinder.

Modern grinder installations are very different in appearance from these old ones, and operate much more efficiently. Continuous magazine grinders have been developed, in which the logs are fed into the grinder on one floor and dropped down through the magazine to the pockets of the grinder on the floor below. Such grinders are usually installed in pairs driven by a motor which may rate as high as 4000 horse power and have a turning speed from 3,500 to 5,000 rpm.

The increasingly popular disk mill method uses a refiner to shred and grind groundwood chips between counter-rotating metal shearing disks. Refiner-ground wood, which usually has longer fibers, is preferred over stoneground wood since it yields a stronger paper.

Both types of mechanical pulpers are generally used in an integrated papermaking facility, in which the resultant fiber is thickened by removal of water and stored as slush pulp rather than being formed into flat sheets for sale as market pulp. Characteristically, groundwood pulping requires high power - over 32,000 kw to operate a 500 ton per day groundwood mill.

Unlike chemical pulping, groundwood pulping entails considerable fiber damage. It produces a relatively weak paper that discolors easily on exposure to light. On the other hand, groundwood processes have the advantage of converting about 95 percent of the dry weight of wood into pulp, compared to about 50 percent for chemical processes. The strength problem may be overcome by adding long-fibered chemical pulp to groundwood pulp between the pulping and papermaking stages.

Groundwood pulp constitutes 70 to 80 percent of newsprint by weight. Groundwood plants are principally located in Canada and the southern U.S., where the supply of softwood and electricity is ample.

2.2.2 Chemical Pulping

Chemical pulping is the process of cooking wood with suitable chemical reagents to dissolve and degrade the lignin, the cementing material between the wood fibers, and allow the fibers to be easily separated. The diversity of pulping processes is increasing in response to the availability of improved technology, the need to improve productivity, and the requirement to curb pollution. Currently, two major chemical techniques and one semichemical technique of widespread commercial importance are employed.

The most significant chemical processes are the sulfate or kraft process, the acid sulfite process, and the neutral sulfite process. In the kraft and the acid sulfite processes, the debarked and chipped wood is loaded into a large metal digester along with the appropriate chemicals in an aqueous solution. Heat is applied and cooking is continued, usually at high temperatures and pressures, until the desired degree of delignification and purification is obtained. Cooking transforms lignin, some carbohydrates, resins, and mineral matter into soluble compounds that can be removed by washing. For most pulp grades, over 95 percent of the lignin is eliminated. Because the cooking liquid also attacks and removes some desirable hemicellulose and cellulose from the wood, relatively poor yields are inherent in chemical pulping.

The type of process and products involved determines the necessary cooking conditions. The important variables are the size and physical properties

of the chips, the liquor composition and concentration, and the time, pressure, and temperature of cooking. The liquor concentration is the most important variable since it affects the reaction rate and cooking time; a large initial concentration increases the reaction rate but decreases the yield since the stronger liquor removes or weakens more of the desirable cellulosic materials. From an economic standpoint, the most important variables in cooking are the chemical composition and the thermal energy requirement. The industry is concentrating on improved methods of recovering and recycling the chemicals and of reducing energy inputs.

The acid sulfite process, discovered in 1874 and well established commercially by 1890, remained the most important chemical process until it was overtaken by the kraft process in 1937. Here, the cooking liquor is made at the mill by burning sulfur in air to form sulfur dioxide and reacting the gas with limestone to produce a cooking acid of the desired composition and concentration.

For years the only base used was inexpensive calcium, but sodium, magnesium, and ammonia-based sulfite liquors have come into use recently, especially in Scandinavia and North America, for various reasons: reduced cooking time, easier recovery of cooking chemicals, reduced stream pollution, more marketable by-products, fewer required screenings subsequent to cooking, and greater brightness. However, the soluble bases other than calcium cost four to five times more per ton of pulp and their advantages in yield, reduced cooking time, and improved pulp quality alone, without the possibility of spent liquor recovery and before the advent of stringent pollution controls, would not have warranted industry use.

Since the spent liquor in the calcium-based process is uneconomical to recover and presents a major water pollution control problem, most plants will abandon the process unless an economical way can be found to recover or dispose of the spent liquor. Spent liquor has been variously used, e.g., as a road binder or in the manufacture of yeast, vanilla, alcohol, fertilizers, insecticides, tanning agents, and inks. It can also be burned in concentrated form to produce power and steam; the heat value of the dried sulfite waste is about two-thirds that of industrial coal, but much of the energy produced must be used to evaporate and con-

centrate the liquor in preparation for burning. Even this limited recovery is likely to become more attractive as energy prices rise.

Despite such efforts to find alternative uses for the spent liquor, most mills have continued to dispose of it as a waste product. Recent water pollution control requirements might alter this trend.

The kraft (sometimes called the sulfate) process is now predominantly used in pulping. The name "sulfate" (derived from the sodium sulfate used as the make-up chemical in the chemical recovery process) is misleading since the active cooking agents are mostly sodium hydroxide and sulfide.

As in the sulfite process, wood in chip form is cooked in large steel digesters in the presence of a cooking liquor and under conditions of elevated temperatures and pressures. The cooked chips are then defiberized in a blow tank and screened as necessary before washing and bleaching. The prepared pulp may be either pressed and dried into flat sheets for sale or shipment to another facility or retained in a slurry form for use at an adjoining paper or paperboard plant.

The kraft process has various advantages: it can be used on almost any species or quality of wood; its cooking times are short; it entails no pitch problems; recovery of the spent liquor is relatively easy; and it yields valuable by-products. The pulp produced has great strength and can be bleached to high levels of brightness. The efficient chemical recovery system is especially advantageous and economical since the sodium hydroxide used in the kraft process is a very effective but relatively expensive chemical.

The principal disadvantages of the process are its high capital costs, high cost of bleaching, and discharge of several highly malodorous waste gases (e.g., hydrogen sulfide). Regulations requiring controlled discharge are thus significantly affecting the economics of the kraft process. Electrostatic precipitators and scrubbers are being used to reduce odor by precipitating dust particles to which the odor producing particles cling. Unfortunately, since the wastewater from these cleaning operations cannot be used for pulp washing because the odor is imparted to the pulp, this deodorizing method merely substitutes a liquid waste problem for a gaseous one.

2.2.3 Semichemical Pulping

Semichemical pulping, which combines mechanical and chemical pulping features, chemically treats the wood to achieve partial softening and then uses mechanical refining to complete the fiberization. Semichemical pulping offers several advantages over both chemical and groundwood processes. The yield is from 65 to 90 percent of the weight of the wood because only part of the lignin and hemicellulose is removed. This is considerably better than the straight chemical process. The chemical pretreatment reduces the amount of power necessary for the subsequent mechanical reduction, increases the average fiber length, and enables the process to be used effectively with hardwoods. In addition, since semichemical pulping uses fewer chemicals than the pure chemical processes and requires a lower capital investment, it lends itself to use in smaller plants. One drawback is that semichemical pulping only works well for hardwood and is not used for softwood species.

The two most important types of semichemical pulping are the neutral sulfite semichemical and the cold caustic processes. The more widely used neutral sulfite process treats the wood with a solution of sodium sulfite which, during cooking, is buffered to about pH 7 with a buffering agent such as sodium bicarbonate. The physical characteristics of the neutral sulfite process pulp make it particularly well suited for use as a corrugating medium. The neutral solution produces a pulp with high yield, about 65-80 percent, strength, and brightness without offensive odors.

The cold caustic process, which employs caustic soda (sodium hydroxide) to produce coarse pulps for corrugating and some finer pulps for printing papers, is particularly useful with high density hardwoods that cannot be used in the groundwood process. Efficient use of chemicals and reduction of the mechanical energy required for subsequent refining make this process lower in operating costs than either groundwood or other semichemical processes. The pulps produced are inferior to kraft pulps in physical properties but stronger than or equal to groundwood pulps made from softwoods.

Chemical recovery in semichemical mills, unlike in the kraft system, can use a number of chemical processes. For the semichemical process

using caustic soda, a recovery process similar to that used to recover sodium hydroxide in the Kraft process may be used. Most of the remaining techniques involve either combustion or cross-recovery (using the kraft mill recovery system).

2.2.4 Secondary Fiber Pulping

Secondary fiber, derived from wastepaper, is a principal source of pulp for some papermaking facilities around the large metropolitan areas. Secondary fiber accounts for about 20% of the fiber used for pulp today. Although the rising cost of fiber will undoubtedly induce the industry to increase use of secondary fiber (especially recycled paper, the highest-quality wastepaper used for making pulp today), such increases may be less than is popularly anticipated. Rising energy costs, the difficulty of separating wastepaper from other trash, and the lack of captive supplies may limit the growth in use of wastepaper as a fiber source. Mills that use wastepaper generally have little control over their secondary fiber supply, although firms are increasingly seeking long-term wastepaper supply arrangements.

2.2.5 Dissolving and Special Pulps

Variations of the basic sulfate and sulfite processes which produce pulps for paper and paperboard are used to produce a special type of pulp called dissolving pulp. This segment of the pulp industry has become so specialized that it operates much as a separate industry. To generate dissolving pulp, pulps produced by kraft or sulfite processes are chemically purified to remove all semi-cellulose and to extract pure cellulose. The pure cellulose is then used as a raw material to produce rayon, cellophane, and cellulose derivatives used in such diverse products as explosives, detergents, lacquer, food product thickeners, hand lotions, and automobile accessories. Dissolving pulp is also used to make glassine paper (the paper that forms the clear window in window envelopes). Dissolving pulp facilities are frequently located adjacent to kraft and sulfite mills so that the pulp can be delivered in slush form without drying.

2.3 EPA Classification of Mills by Pulping Method

It is at the pulping stage that the process schemes allow for differentiation between plants. In compliance with certain sections of FWPCA of 1972, EPA has established the following sub-categories of pulp, paper and paperboard operations for the purpose of establishing effluent guidelines:*

Table 2-1 EPA Mill Classification

1. Bleached Kraft: Dissolving Pulp
2. Bleached Kraft: Market Pulp
3. Bleached Kraft: Fine Papers
4. Bleached Kraft: B.C.T. Papers
5. Papergrade Sulfite
6. Papergrade Sulfite Market Pulp
7. Low Alpha Dissolving Sulfite Pulp
8. High Alpha Dissolving Sulfite Pulp
9. Soda
10. Groundwood: Chemi-mechanical (CMP)
11. Groundwood: Thermo-mechanical (TMP)
12. Groundwood: Fine Papers
13. Groundwood: C.M.N. Papers
14. Deink
15. Non-Integrated Fine Papers
16. Non-Integrated Tissue Papers
17. Non-Integrated Tissue Papers (fwp)

EPA defines each class of mill as follows:

1. BLEACHED KRAFT: DISSOLVING PULP means that production of a highly bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. Included in the manufacturing process is a "pre-cook" operation termed prehydrolysis. The principal product made by mills in this subcategory is a highly bleached and purified dissolving pulp which is used principally for the manufacture of rayon and other products requiring the virtual absence of lignin and a very high alpha cellulose content.

* Reference No. 1; further industry and process descriptions, including wastewater characterization, can also be found in this and associated references.

2. BLEACHED KRAFT: MARKET PULP means the production of bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. Included in this subcategory are mills producing papergrade market pulp as the only product.
3. BLEACHED KRAFT: FINE PAPERS means the production by integrated pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. The principal products made by mills in this subcategory are fine papers which include business, writing, and printing papers.
4. BLEACHED KRAFT: B.C.T. PAPERS means the production by integrated pulp and paper mills of bleached pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. The principal products made by mills in this subcategory are papers of low filler content including paperboard (B), coarse papers (C), and tissue papers (T).
5. PAPERGRADE SULFITE means the production by integrated pulp and paper mills of pulp and paper, usually bleached, by a "full cook" process using an acidic cooking liquor of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The principal products made by mills in this subcategory are tissue and fine papers.
6. PAPERGRADE SULFITE MARKET PULP means the production of pulp, usually bleached, by a "full cook" process using an acidic cooking liquor of sulfite of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The principal product made by mills in this subcategory is papergrade market pulp.
7. LOW ALPHA DISSOLVING SULFITE PULP means the production of highly bleached and purified pulp by a "full cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The pulp produced by mills in this subcategory are viscose, nitration, or cellophane grades and are used principally for the manufacture of rayon and other products requiring the virtual absence of lignin.
8. HIGH ALPHA DISSOLVING SULFITE PULP means the production of highly bleached and purified pulp by a "full cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide.

The pulp produced by mills in this subcategory is principally acetate grade and the principal-uses are for the manufacture of rayon and other products requiring the virtual absence of lignin.

9. SODA means the production by integrated pulp and paper mills of bleached pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide cooking liquor. The principal products made by mills in this subcategory are printing, writing, and business papers.

10. GROUNDWOOD: CHEMI-MECHANICAL means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing a chemical cooking liquor to partially cook the wood followed by mechanical defibration by refining at atmospheric pressure. The principal products made by mills in this subcategory are fine papers, newsprint, and molded fiber products.

11. GROUNDWOOD: THERMO-MECHANICAL means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, by a brief cook utilizing steam, with or without the addition of cooking chemicals such as sodium sulfite, followed by mechanical defibration by refiners which are under pressure. The principal products made by mills in this subcategory are fine papers, newsprint, coarse papers, and tissue products.

12. GROUNDWOOD: FINE PAPERS means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. The principal products made by mills in this subcategory are fine papers which include business, writing, and printing papers.

13. GROUNDWOOD: C.M.N. PAPERS means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. The principal products made by mills in this subcategory are papers of low filler content including coarse papers (C), molded fiber products (M), and newsprint (N).

14. DEINK means the production of pulp and paper usually brightened or bleached from recycled waste papers in which an alkaline treatment is used to remove contaminants such as ink and coating pigments. The principal products made by mills in this subcategory are printing, writing and business papers, tissue papers, and newsprint.

15. NON-INTEGRATED FINE PAPER means the manufacture of fine papers by non-integrated mills from wood pulp or deinked pulp prepared at another site. The principal papers made by mills in this subcategory are printing, writing, business, and technical papers.

16. NON-INTEGRATED TISSUE PAPER means the manufacture of tissue papers by non-integrated mills from wood pulp or deinked pulp prepared at another site. The principal products made by mills in this subcategory are facial and toilet papers, glassine, paper diapers, and paper towels.

17. NON-INTEGRATED TISSUE PAPERS (FROM WASTE PAPER) means the manufacture of tissue papers by non-integrated mills from recycled waste papers (fwp). The principal products made by mills in this subcategory are facial and toilet papers, glassine, paper diapers, and paper towels.

The effluent limitations and standards for the above subcategories are based upon on-site manufacture of all of the pulp (including deinking of waste paper) used to produce the final products (i.e., no supplementary fiber source such as purchased pulp or waste paper was included in the determination of the effluent limitations or standards). The exception to this is the Groundwood: OMN Papers and Groundwood: Fine Papers subcategories which were based upon groundwood mills manufacturing papers from pulp produced on-site and from purchased pulp used as supplementary fiber.⁽¹⁾ Of particular interest from the standpoint of PCBs and waste paper recycling are categories 14, 15, 16 and 17.

2.4 Papermaking Processes

2.4.1 Background

For most paper and paperboard products, the papermaking machine receives prepared paper stock containing about 199 pounds of water for every pound

of dry material, passes it through a series of operations to form it into a continuous web and to remove the excess water, presses the wet sheet to remove still more water and to make the sheet still more dense, dries it over heated driers and finally reels it up into large rolls. This change from stock containing almost ten tons of water per 100 pounds of dry matter to a sheet of paper which seldom contains over 5 pounds of water in 100 pounds of dry paper takes place in just a few minutes according to the speed of the machine. A schematic of the overall process is shown in Figure 2-1.

Although many mechanical variations and improvements have been made over the years, only two basic types of paper machines, the fourdrinier and the cylinder, are used today. Both were invented over a century ago. These machines differ significantly in the method of forming the fiber web.

The fiber stock is subjected to a series of refining and cleaning stages prior to its introduction to the paper machine. These stages are chosen to produce the desired fiber characteristics to meet the product's needs. The fiber stock is mechanically refined in heaters or continuous refiners to fray or "brush" the individual fibers. The frayed fibers will have a tendency to mat together and the degree of matting will produce the required strength in the final paper. In fine papers where a compact, tight mat is required the stock may also be pumped through a fordan which will cut the fibers to the required length with a limited amount of brushing.

2.4.2 Fourdrinier Paper Machine Process

In the fourdrinier, the refined stock is pumped to a headbox which controls the amount of stock flowing to the paper machine "wire" and thus maintains the paper at the desired consistency. The carefully diluted stock (~ 0.5% solids) is then spread evenly on the "wire" (a woven brass or bronze cloth, the mesh of which differs in type and size of opening according to the paper being made) to form the paper. Water drains through the wire, and is squeezed from below to assist in the drainage. The transfer of the sheet to presses is accomplished with a suction pick-up roll. The sheet leaves the "wet-end" of the machine at a consistency of 35 to 40% solids and is passed through heated, hollow iron or steel drum dryer rolls in the dry end. Because of its higher output speed and greater versatility the fourdrinier is more common than the cylinder.

Figure 2-1 gives a schematic process flow diagram for the fourdrinier paper machine. Of special interest is the recycling loop of both water and fiber from the fourdrinier section back to the rich white water tank, saveall and filtered white water tank. This stream is the major inplant carrier of fines-related PCBs, and is shown to be repeatedly passed through the fourdrinier to incorporate as much of the fiber and fines load as possible in the product paper.

2.4.3 Cylinder Paper Machine Process

In the cylinder machine, the headbox and wire found in the fourdrinier are replaced by a wire-covered cylinder mold which is partially immersed in the prepared stock.

The principle of the cylinder machine differs from that of the fourdrinier in several respects. Instead of the sheet being formed on an endless belt of woven wire through which the water drains, leaving the fibrous stock on its surface, the cylinder mold revolves while partially immersed in a vat of the dilute stock and the sheet is formed on the surface of the wire-covered mold. This is accomplished by maintaining the water level within the cylinder lower than that outside so that the water drains into the cylinder leaving the stock on its surface. The web of paper formed by the revolving cylinder is removed off the top of the cylinder by a felt. Usually a cylinder machine consists of several cylinder molds and vats supplied with stock entirely independently, and as the felt passes over each cylinder in turn it picks up the sheet from each, thus making a sheet of multiple layers. This makes it possible to form sheets with surface layers differing from those within the sheet, either in color, kind or fiber or both.

The same basic flow process is associated with cylinder machine as the fourdrinier shown in Figure 2-1; however, as mentioned above, the final product may be multi-layered, requiring a parallel stock flow through each cylinder machine.

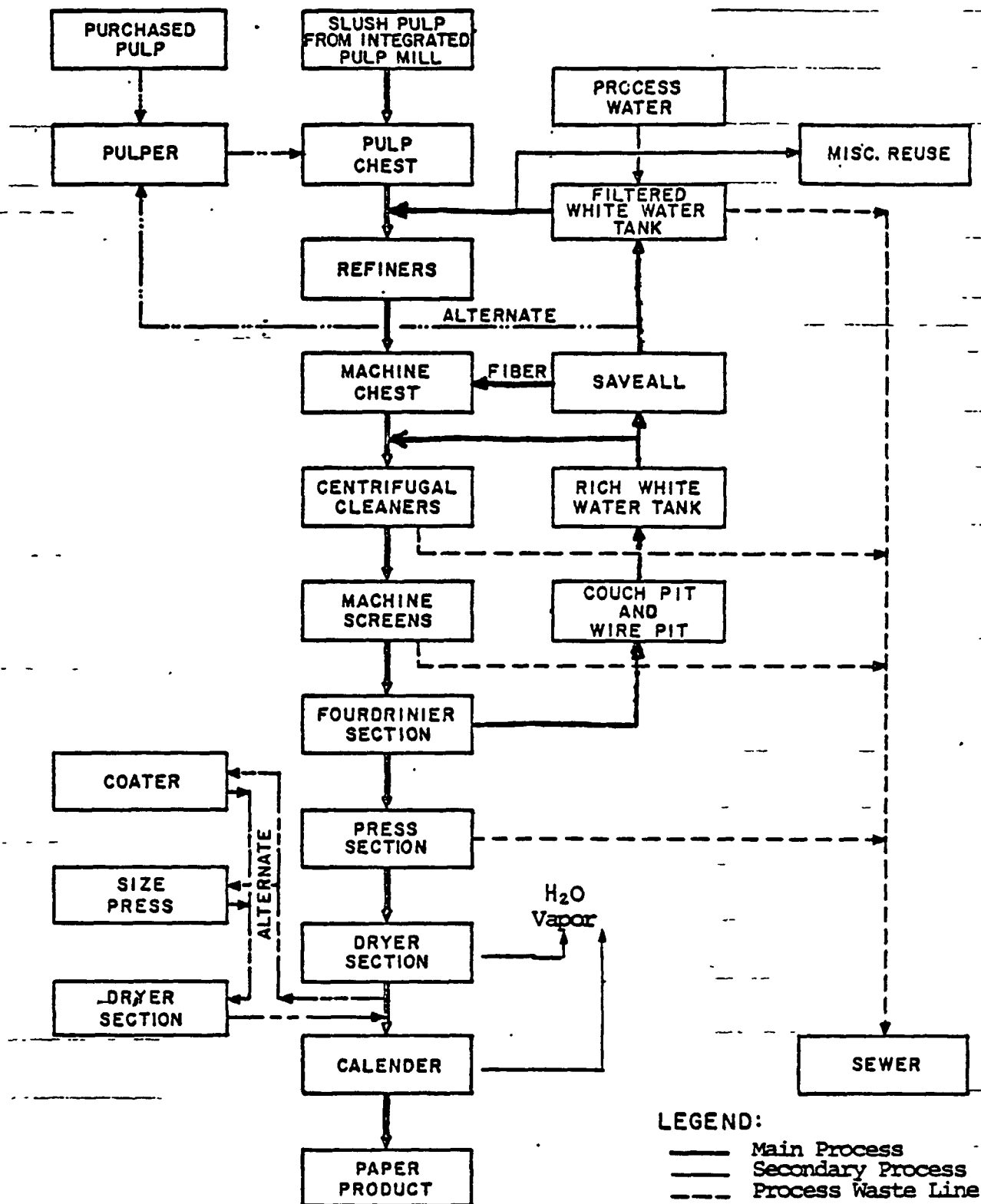


Figure 2-1

GENERALIZED SCHEMATIC OF PAPER PRODUCTION PROCESS

2.5 Paper Industry: Size and Distribution

2.5.1 Water Usage

Census Bureau data shows that Paper and Allied Products had a 1973 water intake of 2,415 billion gallons. Gross water usage was estimated to be 8,126 billion gallons. The ratio gross/intake shows how much water re-use is occurring. The historical trend is shown on Table 2-2.

Table 2-2
Water Usage in Paper and Allied Products Industries

<u>Year</u>	<u>Gross Water (billion gal)</u>	<u>Intake Water (billion gal)</u>	<u>Gross/Intake</u>
1973	8127	2415	3.36
1968	6522	2252	2.89
1964	5491	2064	2.66
1959	5046	1937	2.60
1954	4242	1786	2.38

Between 1954 and 1973 water intake increased by 35%. In the same period, total paper and paperboard production rose 106%. The trend to internal water recycling is well documented and continuing. A report by Rapson⁽²⁾ describes the processes to be used at the bleached kraft mill of Great Lakes Paper Co., Ltd. at Thunder Bay, Ontario. This mill will start up in late 1976 and will recycle virtually all of its water, emitting only low temperature heat in uncontaminated cooling water. Projections indicate this to be at a lower cost than use of external treatment. One major reason will be the conservation of heat in the counter current washing of the bleached pulp.

Allowing for a 5% water loss associated typically with product moisture, about 2.2 trillion gallons of water was discharged to U.S. waterways in 1973. Average runoff for the continental U.S. is given by Todd⁽³⁾ as 655 trillion gallons. A simple division indicates that the paper and allied product discharge is 0.33% of the total continental runoff. Since the discharge is not evenly distributed over the rivers, the water quality of even large streams can be strongly affected by the effluent loads from paper mills.

2.5.2 Production History

There is much potential for confusion in the utilization of data from the pulp and paper industry because over the years for which information has been retained, new products as well as new processes have appeared. As a result, the categorization of the output of the industry is constantly changing. While the categories are relatively stable over a short term period, they have changed noticeably during the long term. The general overall trend has been one of production increase, underlain with a use of recycled waste paper which has varied with world economic and political conditions. Table 2-3 shows the information on production and secondary fiber usage obtained from Bureau of Census, American Paper Institute and other sources for the 1957-1974 period.

According to the last column of Table 2-3, the rate of recycling has remained virtually constant at about 20% since 1968. Even with the emphasis on re-use and conservation of natural resources, little change can be seen. Lingle⁽⁴⁾ states that paper constitutes 31% by weight of municipal solid wastes going to disposal. Of that paper, 29% is corrugated containers, newspapers and printing papers are each 20%, and packaging and the other categories make up the balance. Slightly more than half of all paper wastes are from residences with the rest originating in commercial or institutional locations.

Source separation is a basic part of most collection systems focusing on recycling. Newspaper bundling in residential areas and compacted corrugated carton collection from commercial establishments are examples of such source separation schemes. This is required so that a paper mill utilizing recycled paper in its furnish (raw material) can be assured that the proper type of fiber is going into its process.

The type of catch-all waste which emanates from offices, government and commercial firms is termed "mixed waste". While it can be utilized by segments of the paper industry, there exists the chance in this waste stream for the carbonless copy paper which contains PCBs.

TABLE 2-3

Product Output and Recycle Rate

<u>Year</u>	<u>Paper (10⁶ tons)</u>	<u>Paperboard (10⁶ tons)</u>	<u>Construction Board (10⁶ tons)</u>	<u>Output Total (10⁶ tons)</u>	<u>Paper Stock Recycled (10⁶ tons)</u>	<u>% Production Recycled</u>
1957	13.6	14.1	3.0	30.7	8.5	27.7
1958	13.5	14.1	3.2	30.8	8.7	28.2
1959	15.0	15.5	3.5	34.0	9.4	27.6
1960	15.4	15.7	3.4	34.5	9.0	26.1
1961	15.7	16.4	3.4	35.6	9.0	25.2
1962	16.5	17.5	3.4	37.5	9.1	24.3
1963	17.3	18.2	3.7	39.2	9.6	24.5
1964	18.2	19.6	3.9	41.7	9.8	23.5
1965	19.2	20.8	4.1	44.1	10.2	23.1
1966	20.7	22.6	3.9	47.1	10.6	22.5
1967	20.9	22.1	3.9	46.9	9.9	21.1
1968	22.4	24.5	4.3	51.2	10.2	19.9
1969	23.6	26.1	4.5	54.2	10.9	20.1
1970	23.6	25.5	4.4	53.5	10.6	19.8
1971	23.8	26.1	5.1	55.1	11.0	20.0
1972	25.4	28.5	5.5	59.5	11.7	19.7
1973	26.5	29.7	5.7	61.8	12.2	19.7
1974	26.9	27.9	5.2	59.9	12.1	20.2

3.0 TRANSPORT OF PCBs IN THE PAPER INDUSTRY

3.1 PCB Sources to the Industry

3.1.1 Influent Waters

A representative value for PCBs concentration in the intake waters of paper mills was deemed necessary for several aspects of the work. This value, which was determined to be 0.1 ppb, was derived from several sources as shown below.

During the early months of 1976, EPA instructed its Regional Offices to conduct a sampling program aimed at identifying point sources of PCBs to the environment. This Regional Surveillance Program reported in excess of 2,400 data points. Of these, 106 could be unambiguously categorized as having come from a natural body of water. With the elimination of a few samples suspected of being contaminated, the average value of these "natural water" samples is 2.3 ppb. However, the choice of sampling sites was usually contiguous to a facility which was already a potential PCB emitter, so that this value is probably more representative of a high use, industrially developed stream rather than an environmental background. The intake PCB concentrations for paper mills might therefore be expected to be somewhat less than this 2 ppb average. Paper mills faced with suspended solids in their intake water will usually perform a clarification clean-up prior to use. Such treatment would be expected to remove up to 90 per cent of the PCBs from the water (retained on removed particulates).

Dennis⁽⁵⁾ obtained STORET data for PCBs in major U.S. drainage basins and showed a range of median values for each basin from ND (not detectable) to 0.3 ppb in his tabulation for 1974.

Data on intake water PCB concentrations from the Institute of Paper Chemistry for eight Wisconsin paper mills showed three mills reporting undetectable levels and the other five reporting an average of 0.2 ppb PCBs.

On the basis of the above considerations, the representative PCBs level of the water used in paper mills was taken to be 0.1 ppb.

3.1.2 Process Chemicals

Table 3-1 gives a typical listing of some of the major kinds of chemicals used in pulp and paper making. The amounts used on a per unit ton basis vary from trace quantities to 280 lbs. for some pulping liquor constituents.

Both Crown Zellerbach and Institute of Paper Chemistry researchers have tested process chemicals for PCBs. None have ever been detected except for one specialty chemical reported by IPC. A rough calculation shows that to produce a 2 ppm PCB concentration in a product which uses 8 lbs. of trisodium phosphate per ton of pulp (assuming a complete extraction of PCB by the fiber), 2 grams of PCB would have to come in with the detergent. Its concentration in the detergent would be 5500 ppm, easily detected. Even an increase of 0.1 ppm in the product from this source would require a concentration of 27.5 ppm in the phosphate. Present analytical capabilities allow monitoring at 1 ppm and below, so that PCB inputs from process chemicals would have been easily noticed.

3.1.3 Inks

The National Printing Ink Research Institute at Lehigh University was contacted for details on present and past usage of PCBs in printing inks. The major use reported was the NCR encapsulation procedure used in the carbonless copy paper. A small number of patents do exist for PCB use as part of some inks sensitive to ultraviolet light. However, they date from the very early seventies and had not gotten into widely marketed use by the time the PCB use in carbonless copy paper was stopped. To the best knowledge of NPRI, none of these inks reached commercial production and no present day formulations utilize PCBs as a constituent.

Subsequent conversation with a representative of the Sun Chemical Co.* indicated that PCBs were used for several years prior to 1971 in "flexographic" inks used on flexible packaging. It was estimated that the production of such inks during 1970 was about 20 million pounds, of which about five per cent of the production would have contained PCBs at a two per cent by weight concentration. Thus, the estimated use of PCBs for this purpose, apparently the maximum, was 20,000 pounds in 1970. The historical trend for this application is not known, but based

*Personal Communication with Mr. William Rusterhaltz, Sun Chemical Co., October, 1976.

TABLE 3-1
REPRESENTATIVE CHEMICALS USED IN PULP & PAPERMAKING

<u>Name</u>	<u>Chemical Symbol</u>	<u>Amount lbs/Ton Pulp</u>	<u>Uses/Remarks</u>
Ammonia	NH_3	90-120	Sulfite pulping
Nitric Acid	HNO_3		Nitric acid pulping
Sodium hexametaphosphate	$\text{Na}_{16}\text{P}_{14}\text{O}_{113}$	2-4	Pitch dispersant for sulfite pulp
Sodium tripolyphosphate	$\text{Na}_3\text{P}_3\text{O}_{10}$	10	Sequesterant for brightness
Trisodium phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	4-8	Dinking detergent
Sodium Sulfate	Na_2SO_4		"Salt cake", Kraft pulping make-up
Sodium pentachlorophenate	$\text{C}_6\text{Cl}_5\text{ONa}$		Slime control
Sodium Sulfite, anhydrous	Na_2SO_3	140-280	Cooking liquor for neutral sulfite semi-chemical pulping
Sodium Acid Sulfite	NaHSO_3		Buffer, removes residual chlorine from bleached pulp
Sodium Carbonate	Na_2CO_3		Dinking, "soda ash"
Surfactants	Dodecylphenol of ethylene	10-15	Dereasination of pulp
	Oxide bases	4-8	Dinking and defibration of waste paper
Sulfur Dioxide	SO_2		Bleaching
Sulfuric Acid	H_2SO_4		pH control, reducing agent for NaClO_2
Aluminum chloride	AlCl_3		Alum replacement
Sodium hydroxide	NaOH		Bleaching, dinking, "caustic soda"
TCC	3,4,4 trichlorocarbonyl chloride		Bacteriostat (microbiological control) substantive to cellulose
Hydrochloric acid	HCl		pH adjust, cleaning agent
Orthodichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$		Cleaning solvent for felts
Phosphoric Acid	H_3PO_4		Brightener, precipitates Ca. & phosphate
Miscellaneous			A large number of special purpose additives; sweeteners like saccharin, odorants like ethyl vanillin, and so on.

on a five-year period of usage and linear growth during that period, it is estimated that the total usage of PCBs in such inks was about 50,000 lb.

The above figure is roughly 0.1 per cent of total PCBs usage in carbonless copy paper. In addition, flexible packaging materials typically were plastic or contained plastic adhesives which render them unattractive for recycling. Thus, it appears unlikely that the PCBs usage in flexographic printing inks has contributed significantly to PCBs inputs to the paper industry.

3.1.4 Recycled Waste Paper

As was indicated in Section 1.0, the major source of PCBs entry into the paper industry appears to have resulted from the use of Aroclor 1242 in carbonless copy paper during 1957-71 and subsequent recycling of a fraction of this product. To some extent, PCBs contamination has spread from this source throughout paper products because of the affinity of paper for PCBs. A summary of available data on PCBs levels in various types of paper products, by year, is presented on Table 3-2. The recycling of these products tends to perpetuate the contamination.

3.1.5 Other Potential Uses or Sources of PCBs in Paper Mills

Although paper mills utilize askarel-filled (PCB) transformers and capacitors, and may have utilized PCB-filled hydraulic or heat transfer systems, PCB-containing lubricants, paints, etc., it is considered unlikely that such activities would be causing release of significant quantities of PCBs to either effluent streams or product streams.

Similarly, it is also considered highly unlikely that PCBs are produced in the practice of wastewater chlorination in the paper industry. Biphenyl has not been identified as a waste stream constituent from this industry, although very small amounts could conceivably enter via recycling of packing materials (typically for fruit) which have been treated with biphenyl as a fungicide.

3.2 PCB Content of In-Plant Streams and Reservoirs

Data on PCB levels of in-plant process streams are almost completely nonexistent for three apparent reasons. First, at the observed low concentrations, PCBs have no effect on product quality, so that internal monitoring is not required.

TABLE 3-2

PCB CONTENT OF PAPER AND PAPERBOARD

		No. of Samples	PCB Content (ppm)	Reference
1968	Virgin pulp	2	0.29	6
Prior to 1970	Recycled ⁽¹⁾ wastepaper input	13	3.2	6
1971	Recycled ⁽¹⁾ wastepaper input (1970-1972)	24	1.1	6
1972	Recycled paperboard	200	15.3	7
	Virgin pulp	2	0.16	6
1973	Paperboard	100	0-20	8
1973	Virgin newsprint	3	<.5-1.0	9
	Recycled newsprint	3	<.5-1.38	9
	Virgin bond paper	7	<.5-8.5	9
	Recycled bond paper	2	113.5-290	9
	Bleached kraft pulp	4	<.5-1.33	9
	Bleached kraft liner board	1	<.5	9
	Publication paper	3	<.5	9
1974	Recycled paperboard	115	1.45-2.97	7
	Recycled ⁽¹⁾ wastepaper input	5	0.37	6
	Virgin pulp	2	0.127	
1975	Paperboard	4	0.3-1.2	10
	Virgin pulp	6	0.072	11
1976	Paperboard	-	0.430	11
	Cereal liner	-	0.8	6
	Corrugated board	-	0.2	11
	Waxed paper	-	0.5	11
	Spec. twist	-	0.2	11
	Lamin. grade	-	0.3	11
	Bookstock	-	1.6	11
	Recycled ⁽¹⁾ wastepaper input	138	0.15	6

(1) Discounting known samples of NCR carbonless copy paper.

Second, most plants, especially the older ones, are not planned with specific capability for sampling in-plant flows, so any sampling done is more by opportunity than by design. Thirdly, commercial PCB analyses cost from \$60 to \$100 per sample, and a sampling program without a clear goal of compliance with regulations or product improvement is generally considered a poor investment. A PCB analytical system would require capital costs in the range of \$15,000 to \$20,000 and annual expenditures for trained personnel, lab space, and operation of up to \$50,000.

3.2.1 PCBs in Deinking and Pulping Process Water

The deinking process water is typically not a recycled stream, although in many cases it represents a significant fraction of the total water usage for a recycling mill. Deinking procedures and conditions depend on the product qualities desired (white or natural or color, etc.). Although some of the PCBs associated with recycled paper will probably be stripped from the fibers during deinking, this should represent only a minor fraction of the total PCB load of the reclaimed material.

During the pulping process the cellulose fibers are separated, and this process should also release the PCBs or PCB-containing microballoons held within the mat. PCBs already released from microballoons would then be able to distribute themselves between the fibers and the water. Since evaporation and other losses of PCBs during pulping should be small, the above appears to be the situation when the slush pulp enters the paper mill.

3.2.2 Distribution of PCBs in the Papermaking Process

In the papermaking process (see Figure 2-1), most of the PCBs entering with the pulp exit with the product. These would include most of the PCBs in intact microballoons and most of the PCBs associated with fibers. In the drying and calendaring sections, the vaporization of excess water would be expected to codistill free (not encapsulated) PCBs at or near the surface. This is the major opportunity for vaporization loss in the process.

In a typical plant, much of the water in the papermaking process (white water) is recycled as shown in Figure 3-1. White water from the fourdrinier or cylindrical machines contains dissolved and suspended PCBs. The fibers present

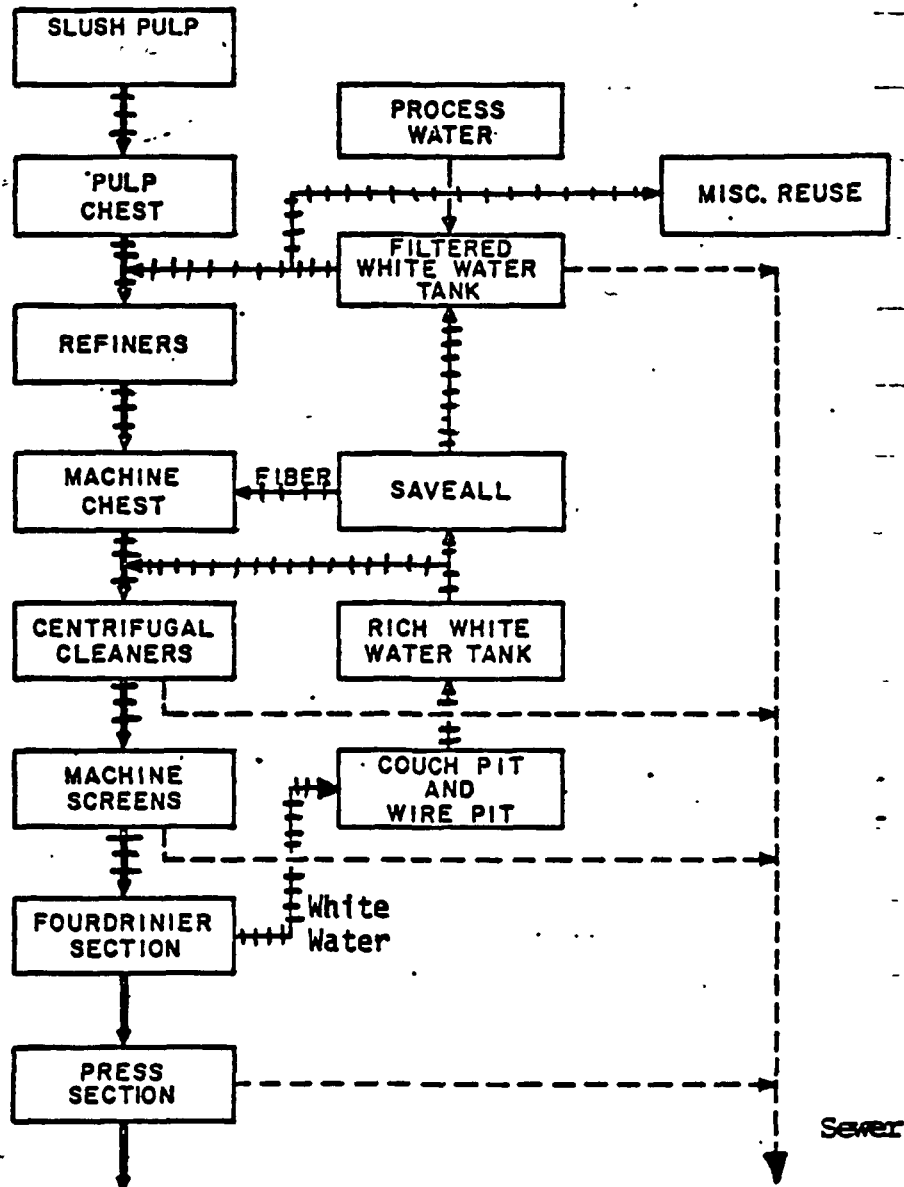


Figure 3-1
Major Fiber and Water Routes in Paper Production

are relatively small, with high surface area per unit weight, so that the ratio of PCBs to solids by weight may be as large as or greater than the PCBs content of the product. Much of the PCBs in suspended form is added back to the main process with the short fibers, in order to conserve fiber. The liquid phase from the "save-all", a separator unit, is filtered to further remove fiber (which goes back into the process) and the filtrate is discharged. This clarified save-all yield can be one of the major components of the discharge from the plant.

If we assume a 1 ppm PCB concentration (typical of product PCB levels using recycled pulp) in the fiber portion of the clarified save-all yield (at 120 mg/l solids), the PCB concentration of that flow is 0.12 ppb which is effectively the same as the intake value selected as representative, and near the lower working limit of present analytical techniques. About 95 per cent of the PCBs entering the save-all appear to be directly recycled back into the paper on the PCBs first pass through the white water system. Thus, it appears that most of the PCBs (and the solids) in the effluents arise from unit processes other than the save-all.

Since it appears that most of the PCBs in paper mill effluents are associated with the fiber solids (either encapsulated or adsorbed PCBs), the major route of PCBs entry into wastewaters must then be via solids entry. On Figure 3-1, this occurs primarily in the aqueous discharges from the centrifugal cleaners, machine screens, and press section. Fiber loss at these points is sufficient to cause solids levels up to several grams per liter in the raw wastewater.

3.2.3 Fate of PCB-Containing Microspheres

The hardened gelatin-gum arabic walls of the ink-carrying microballoons used in the NCR carbonless copy paper are considered essentially stable under conditions typically encountered in the use of secondary fiber. Thus, most of the microballoons should proceed through the process intact. Most would be expected to be incorporated into the product, because of the manner in which fiber is collected in to product (essentially a filtration process).

Based on the above, the PCBs content of the plant effluent should consist of those microspheres not retained in the product and a fraction of that released by breakage (through usage of the paper, during collection and transport of wastes, and in the recycling and papermaking processes). The remainder of that released by breakage could remain on the product, be vaporized, or removed from the stream in various other ways.

This line of reasoning leads to the conclusion that most of the PCBs in paper products and wastepaper is still encapsulated. Discussions with paper industry representatives have supported this view, especially discussions on the comparison of analytical results between procedures in which the microballoon walls have and have not been definitely destroyed. PCB levels resulting from destruction of the microsphere walls with alcoholic potassium hydroxide solution are much higher than those obtained using conventional extraction procedures. However, this could be grossly misleading since the same treatment is necessary to separate the individual fibers to release for analysis PCBs (in whatever state) trapped within the mat.

The actual proportion in paper products and effluents of PCBs in intact microballoons is not known and could be ascertained only with difficulty. One of the items of future work proposed by the Institute of Paper Chemistry in a recent report⁽¹²⁾ is to determine the amount and effect of PCBs present in products and effluents within intact microballoons.

3.3 PCB Losses from the Pulp and Paper Industry

3.3.1 Wastewater

The PCBs content of microballoons in plant effluents can be removed by solids removal; similarly, PCBs sorbed onto suspended solid in the effluent can likewise be removed. Solubilized PCBs, either in true solution or present in or on very small particulates, will be very difficult to remove from effluents.

The partition coefficient for PCBs between cellulose and water is not expected to be anywhere near as large as those between lipids or carbon (for example) and water, based on the relatively slight accumulation in woody plants

and scanty general information available on this subject. Unpublished data obtained from the Institute of Paper Chemistry concerning a series of experiments in which one per cent fiber slurries in water were doped with PCBs (up to 100 ppb), shaken and allowed to settle, and then filtered and analyzed, indicated partition coefficients ranging from 800 to 1700. These values are not sufficiently high to allow removal of dissolved PCBs with suspended solids in mill wastewaters as described below.

At a partition coefficient for PCBs between cellulose and water of 500, and a suspended solids content of two gm/liter, about one-half of the "free" PCBs would be expected to be adsorbed onto the fiber. However, recent industry experience has indicated that removal of over 90 percent of the suspended solids from the wastewaters will also remove over 90 percent of the PCBs, with resulting PCB concentrations in the range of 0.1 ppb to several ppb, well below the reported solubility level of Aroclor 1242. In the absence of other information, this appears to indicate that relatively little of the PCBs in the wastewater is present as dissolved PCBs.

Three alternative explanations for the above appear to be possible:

- (1) The partition coefficient between water and the solids present is very much greater than a few hundred;
- (2) Most of the PCBs present are encapsulated in microballoons and are thus removed in this form along with the other solids; or
- (3) Organic solids added to or present in wastewater treatment systems serve to separate the PCBs from the water.

Alternatives (2) and (3), or a combination of these, appear to be more likely than alternative (1). In all paper mill wastewater treatment systems of which we are aware, polymeric flocculation aids are added in primary treatment and/or the water is subjected to activated sludge secondary treatment. It is well-known that biological sludges exhibit a strong affinity for PCBs and, although the sorptive activity of the polymeric agents for PCB relative to water (and cellulose) is not known, it may be surmised that these agents are better scavengers of PCBs than cellulose. However, alternative (2) (most PCBs still encapsulated) remains a strong possibility until proven otherwise.

The PCB levels in raw wastes from recycling plants vary widely but are typically in the range of 10 to 100 ppb. With current waste treatment practices, this is reduced to a typical range of less than 0.5 ppb to several ppb, with occasional excursions. As a consequence of the recent experience showing PCB removal concomitant with suspended solids removal, compliance with BPCTCA (1977) and BATEA (1983) should result in continuation of the downward trend in effluent PCB levels.

3.3.2 Vaporization Losses

3.3.2.1 Losses During Papermaking

Available information indicates that there may be measurable losses of PCB during the removal of moisture from the paper in the dryer section of the machine. This conclusion was reached on the basis of mass balance studies done on a number of cooperating Wisconsin mills.

We are dealing here with a PCB concentration in a typical paper of only .1 gram per ton. Since the qualitative assessment of the vaporization loss was that it was a few percent of the PCBs present, the loss will not pose a health hazard, nor will it have a significant effect on the conclusions reached in the model of the industry.

3.3.2.2 Losses from Effluent Treatment Ponds

A significant amount of the treatment of papermill effluent occurs in systems open to the atmosphere. Such choices as aerated stabilization basins, ditch aeration, and rotating biological surfaces are designed to provide a greater supply of atmospheric oxygen to the effluent for the purposes of lowering BOD. At the same time an opportunity arises for PCBs to exchange across the solid-liquid and liquid-gas interfaces. No definitive data on these processes for PCB loss are available, but there may be the possibility of exchange mediated by the partitioning of the PCBs in the complex systems.

One expects some exchange based on previously published descriptions of apparent losses from natural water systems such as Lake Michigan⁽¹³⁾, as well as demonstrated losses from 1 per cent pulp fiber/distilled water slurries

in experiments carried out at the Institute of Paper Chemistry. The latter case showed up to 30 per cent losses from solutions spiked to the 100 ppb concentration.

Quantitative assessment of the evaporative losses from actual treatment facilities will require application of field sampling techniques for airborne PCBs which are still in the development stage.

3.3.3 Incineration Losses

Destruction of PCBs by high temperature incineration is generally regarded as requiring a 2 to 3 second exposure to 2,000°F for "complete" combustion. Shorter contact times or lower temperatures will not allow complete elimination of these stable compounds. Specially designed incinerators have been operated by Monsanto and other firms for the proper decimation of PCB-containing liquid wastes, but typical municipal and industrial incinerators will not destroy PCBs completely.

3.3.3.1 Bark Burning

In those mills which practice barking, the bark is often utilized as a hog fuel in mills which generate sufficient bark to use it to fire a boiler for steam generation. Smaller producers of bark may simply incinerate it along with unsalvageable fiber from other parts of the operation. Like the virgin wood, bark has a PCB content which is essentially nil and results in an extremely tiny emission to the atmosphere under these conditions.

3.3.3.2 Sludge, Spent Liquor and Carbon Burning

On an industry-wide basis there has been a drastic decrease in incineration of these materials. The price of fuel necessary to mix with them has risen to the point where alternative disposal schemes cost less.

Sludge is dewatered and generally landfilled. Its PCB content usually ranges from 4 to 25 ppm, the same range exhibited for municipal treatment plants.⁽¹⁴⁾ As such, it should be subject to the same careful handling as other PCB wastes.

Spent liquor of all types is being internally recycled and refined to reduce the amount of make-up chemical required in the pulping stages. More and more opportunities are being discovered for converting spent liquors into

salable by-products or for conversion to other uses inside the plant. These reasons have led to a great overall reduction of liquor burning throughout the industry.

Charcoal burning has been used in a few instances for the production of carbon. But the extent is not great and one would expect volatilization of any PCBs to have taken place prior to such an activity. As in bark burning, actual measurements of such potential losses are not available.

3.3.4 Solid Process Waste Losses

The industry exhibits an average process loss of 2 to 5 per cent. That is, of the pulp entering the paper machine, 2 to 5 per cent of the fiber by weight does not get incorporated into the product paper. This amounts to 40 to 100 pounds of solids per ton of product that will be incorporated into the sludge. As mentioned in the previous section, the few data for paper mill sludge PCB content shows it to be in the same range exhibited by municipal treatment plant sludges. These considerations predict that an average mill with 100 ton daily production might landfill between 2 and 120 grams of PCBs per day (0.004 - 0.26 lbs.)

The effective mobility of PCBs in the landfill situation is not well described. The EPA Regional Surveillance Program generated 75 samples described as leachates. These were all samples where ground water was determined to have had the opportunity to percolate prior to sampling.

Eliminating three samples known to be directly associated with highly contaminated industrial sites, the average value for the 72 remaining samples is 2.8 ppb. It is only 2.8 times the 1 ppb detection limit specified in the EPA 40 CFR PT.136 standard analytical method.

Assuming that landfills are about 40 to 50 per cent paper, neither the paper or the sludge would appear to be mobilizing large quantities of PCBs. In fact, the leachate PCB concentration is indistinguishable from that of industrial intake waters reported by the Regional Surveillance Program and described in Section 3.1. The binding of the PCBs to the fiber may be similar in stability and strength to their association with soil or sediment particles. PCB mobility in sediments is reported to be very low.^(15,16,17) This is thought to be due to the availability of organic material with which PCBs preferentially associate.

3.3.5 PCB Concentration in Finished Product

Product concentrations are referred to elsewhere. In general, PCB levels of current products made with recycled fiber range up to one to two parts per million. This material appears to be almost entirely due to use of Aroclor 1242 in NCR carbonless copy paper prior to the spring of 1971. Levels in products appear to be consistently decreasing since the 1971-72 time frame.

3.4 Monitoring Technology

The study of PCBs within the pulp and paper industry is naturally based on the data generated by the analytical procedure. At the present time, just as in the analysis of natural waters for PCBs, there is no standard method for the analyses of pulps or effluents which take into account the peculiarities of the matrices involved. For example, in the analysis of pulp or paper, it is absolutely essential to remove the PCBs from the fiber quantitatively so that eventual extraction into an organic solvent such as hexane may be accomplished. Removal procedures such as treatment with alcoholic potassium hydroxide have been used. Application of surfactants such as Triton X-100 is also practical. Having removed the PCBs from the fiber, it is then necessary to make sure that both forms, the free PCB and the encapsulated PCB from NCR carbonless copy paper, are extracted into the solvent.

There exists a definite problem with storage of samples prior to extraction and analysis. Apparently, the organic activity of the bacterial population immobilizes PCBs in slimes deposited on container walls and fiber. An attempt to control such losses has been to add formaldehyde to the samples, killing all biotic activity. This has proven successful in lake and stream waters.⁽¹⁸⁾

EPA researchers recommend that the extraction step be performed on a vortex mixer in the original container. This is to give the solvent the maximum opportunity to react with any of the analyte bound to the container walls. It also will assist in reducing volatilization losses already shown to be potentially large by the Institute of Paper Chemistry.⁽¹²⁾ Similarly, it has been recommended that all transfers of material during the pre-analysis manipulations be kept to an absolute minimum.

Limited intercalibrations have shown the drastic effects on precision and accuracy which the small differences in sample handling and storage can have. One IPC study showed 3 laboratories reporting 21.5 ppb, 102 ppb and 180 ppb on a split effluent sample. But while other samples showed as large percentage differences, there was no regularity in the laboratories reporting high or low on a given sample. IPC and others are working in the vicinity of a 0.1 ppb detection limit in effluent samples. Most of these intercalibrations took place at concentrations far above the detection limits so noise in the analysis is small compared to irregularities introduced by storage and handling.

Quantitation of the chromatogram is a difficult process for the complex, multi-peaked plots given by PCBs. Paper mill effluents often show interfering peaks caused by non-PCB materials. Recourse to mass spectroscopy analysis is sometimes necessary to separate these interferents. Some removal is accomplished by sample oxidation with chromium trioxide, but many peaks can remain and a qualitative assessment of the chromatogram by a trained person must be employed. The possibility of mis-identification is real, but the alternative use of the GC-mass spectrometer is often too expensive to be considered for routine use.

The continuing decline in PCB concentrations in effluent, sludge and product will require a continuing improvement in detection limits and sample treatment techniques.

A detailed treatment of analytical techniques for PCBs in paper products and paper mill effluents is presented in Reference (12).

4.0 COST DEVELOPMENT OF PCB REMOVAL FROM PAPER RECYCLING MILL EFFLUENT STREAMS

4.1 Background

The major apparent cause of PCBs in this industry is the use, until 1972, of Aroclor 1242 in carbonless copy paper. A significant portion of this paper has gone through at least one recycle resulting in the PCB contamination of the effluents emanating from these facilities.

Three major types of paper recycling mills currently exist in the U.S. They are:

- (1) Mills producing paper products with deinking process;
- (2) Mills producing paperboard from wastepaper; and
- (3) Non-integrated mills producing tissue paper from wastepaper without deinking.

A number of mills in the paper recycling industry are so-called complex mills, i.e., mills which produce multiple paper grades. The basis used for classifying complex mills is the product and process which account for the largest daily production capacity. Table 4-1 summarizes the distribution and the production of the paper recycling industry in the U.S.

The general process used in the paper recycling industry is pulping and deinking (only for deink mills), pulp washing, bleaching (not for paperboard mills), screening and cleaning, and papermaking. PCBs can be released from the recycled paper in any or all of the above process steps. The water usage of a deinking plant is large and can amount to 65 percent of the total usage of the entire mill. Water used in pulp washing is generally done in a counterflow system which allows maximum potential for water reuse. Some characteristics of the effluent streams are shown in Table 4-2. Data on the PCBs level in the effluent streams for this industry are discussed in Section 3.3.

Technologies for the removal of PCBs from industrial wastewaters were evaluated and described in a previous report.⁽¹⁹⁾ Carbon adsorption in conjunction with pretreatment (equalization and multimedia

TABLE 4-1

SUMMARY OF DISTRIBUTION AND PRODUCTION
OF THE PAPER RECYCLING INDUSTRY¹

<u>Category</u>	<u>No. of Plants in U.S.</u>	<u>Annual U.S. Production</u> kkg (ton)/yr	<u>Annual Average Plant Production</u> kkg (ton)/yr.
1. Deink	17	1,000,000 (1,100,000)	58,800 (64,600)
2. Paperboard from wastepaper	165	6,900,000 (7,600,000)	41,800 (45,900)
3. Non-integrated tissue papers from wastepaper without deinking	Not Available ³	Not Available ³	11,680 (12,800) ²

¹Source - EPA reports 440/1-76/047-a and 440/1-74/025-a²Average of 4 plants³There are a total of 72 non-integrated tissue mills in the U.S. with total capacity of 6,300 kkg/day (6,900 tons/day). No information was obtained as to how many plants actually recycle wastepaper

TABLE 4-2

EFFLUENT CHARACTERISTICS OF THE
PAPER RECYCLING PLANTS¹

<u>Category</u>	<u>Effluent Flow Rate</u>	<u>[BOD], mg/l</u>	<u>[TSS], mg/l</u>
	1,000 l/kg of product (1,000 gal/ton)		
1. Deink	range, 55.5 (13.3) - 93.0 (22.3)	40 - 197	45 - 141
	average, 74.0 (17.8)	92	97
2. Paperboard from wastepaper	range, 5.0 (1.2) - 68.4 (16.4)	9 - 82	40 - 83
	average, 30.0 (7.2)	46	164
3. Non-integrated tissue paper from wastepaper	range, 27.9 (6.7) - 79.2 (19.2)	146 - 411	Not available
	average, 53.6	279	Not available

¹Source - EPA reports 440/1-76/047-a and 440/1-74/025-a.

filtration) was recommended as the best current candidate for the removal of PCBs from the wastewaters to the 1 ppb level or below. Cost information generated in this report for the treatment of paper recycling mill effluents is based upon the pretreatment and carbon adsorption cost curves of Figures 4-1 and 4-2 which were taken from that report. (19)

In the analysis which follows, we have taken the general view that sufficient PCBs will be present in solution in the wastewater to warrant consideration of carbon treatment down to the one ppb level. As was discussed previously, it is conceivable that a sufficient fraction of the PCBs present will be removed with the solids during filtration so that the one ppb can be reached without resort to further treatment by carbon or any other technique (uv-ozone, etc.). Similarly, we have assumed, for the purpose of cost estimation, an end-of-pipe treatment without regard to any treatment (to reach BPTCA, etc.) already in place. In essence, then, the following should represent a worst-case situation.

4.2 Plant PCB Wastewater Treatment

The treatment system designed to remove PCBs from wastewater is capable of handling all possible contaminated flows. A schematic flow diagram for this treatment system is given in Figure 4-3. Since there can be a wide variation existing in these flows, a flow equalization basin is necessary to provide a near constant flow downstream to any downstream treatment unit operation.

In the equalization basin, suspended oils and immiscible solvents will separate and rise to the surface. Suspended solids will either rise, fall or remain suspended depending on their densities and particle size. It has been found that suspended solids will absorb PCBs on their surface and these are removed either in the equalization basin or by the subsequent filtration. Any heavy material collected from the bottom of the basin would be drummed and sent to an incinerator for decomposition of PCBs. The floating liquids would be removed by a belt skimmer and drummed for subsequent incineration, since these oils could contain high concentrations of PCBs. It is assumed that PCBs will enter the equaliza-

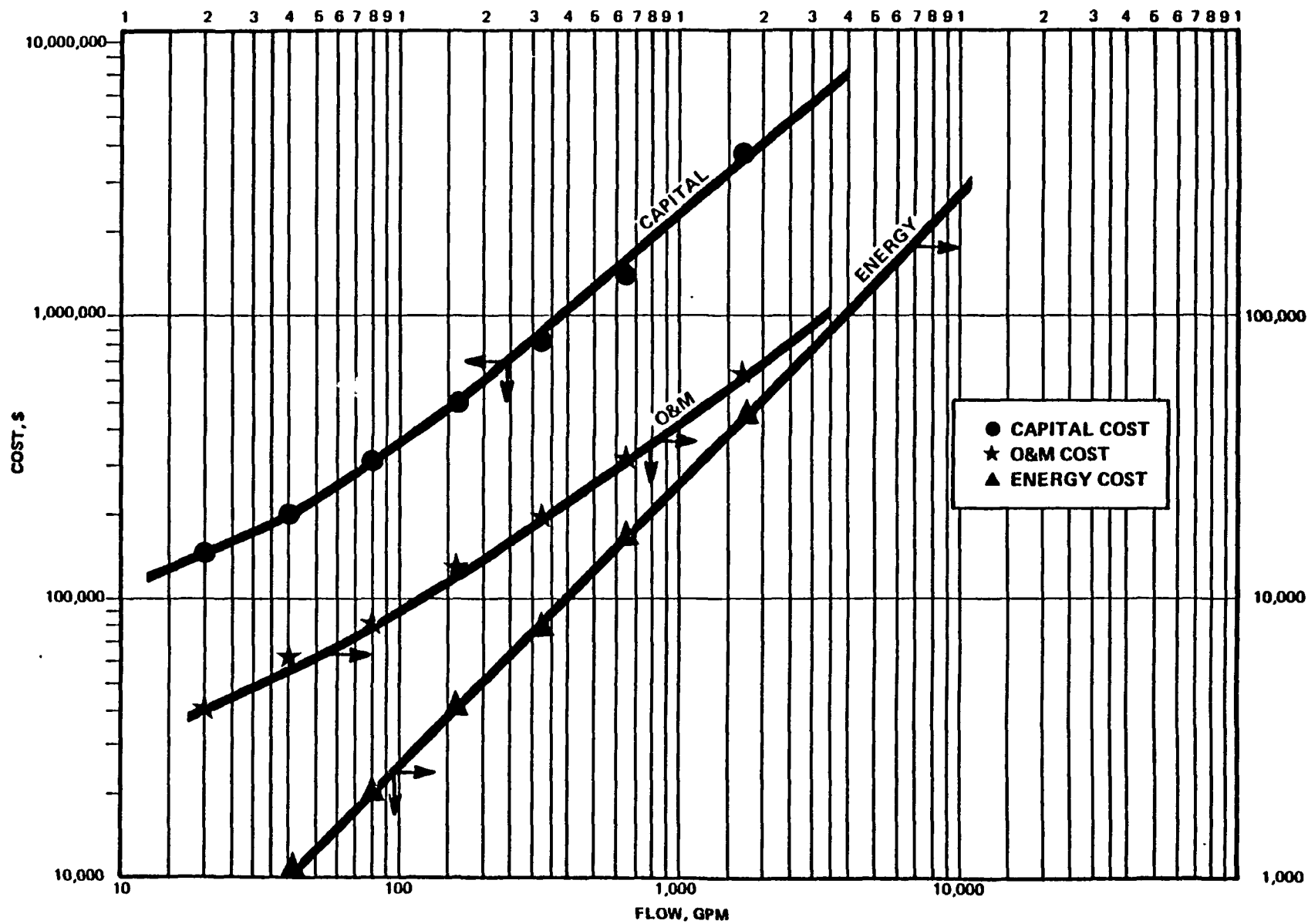


Figure 4-1. PRETREATMENT SYSTEM COSTS

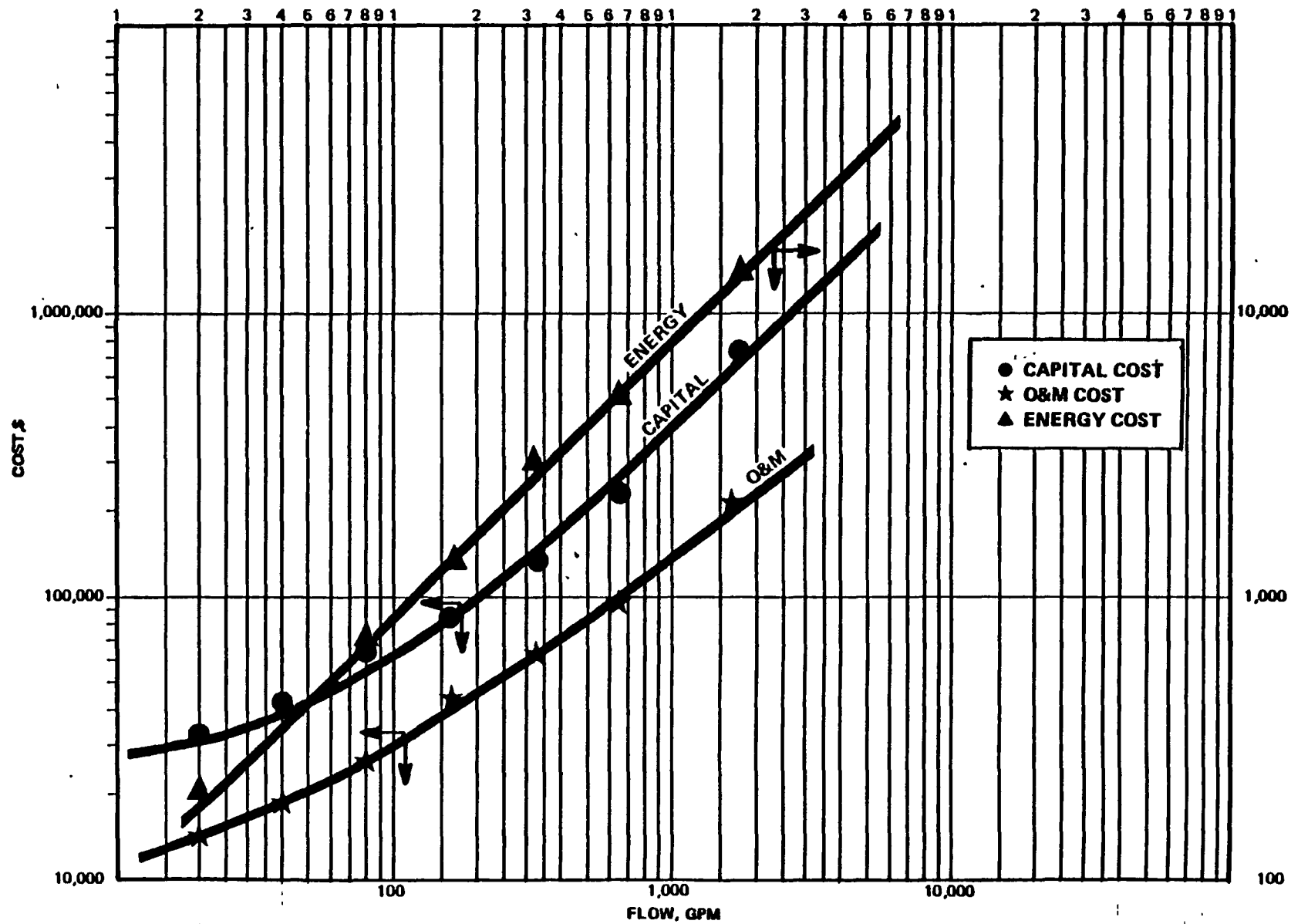


Figure 4-2. CARBON ABSORPTION WASTEWATER TREATMENT SYSTEM COSTS

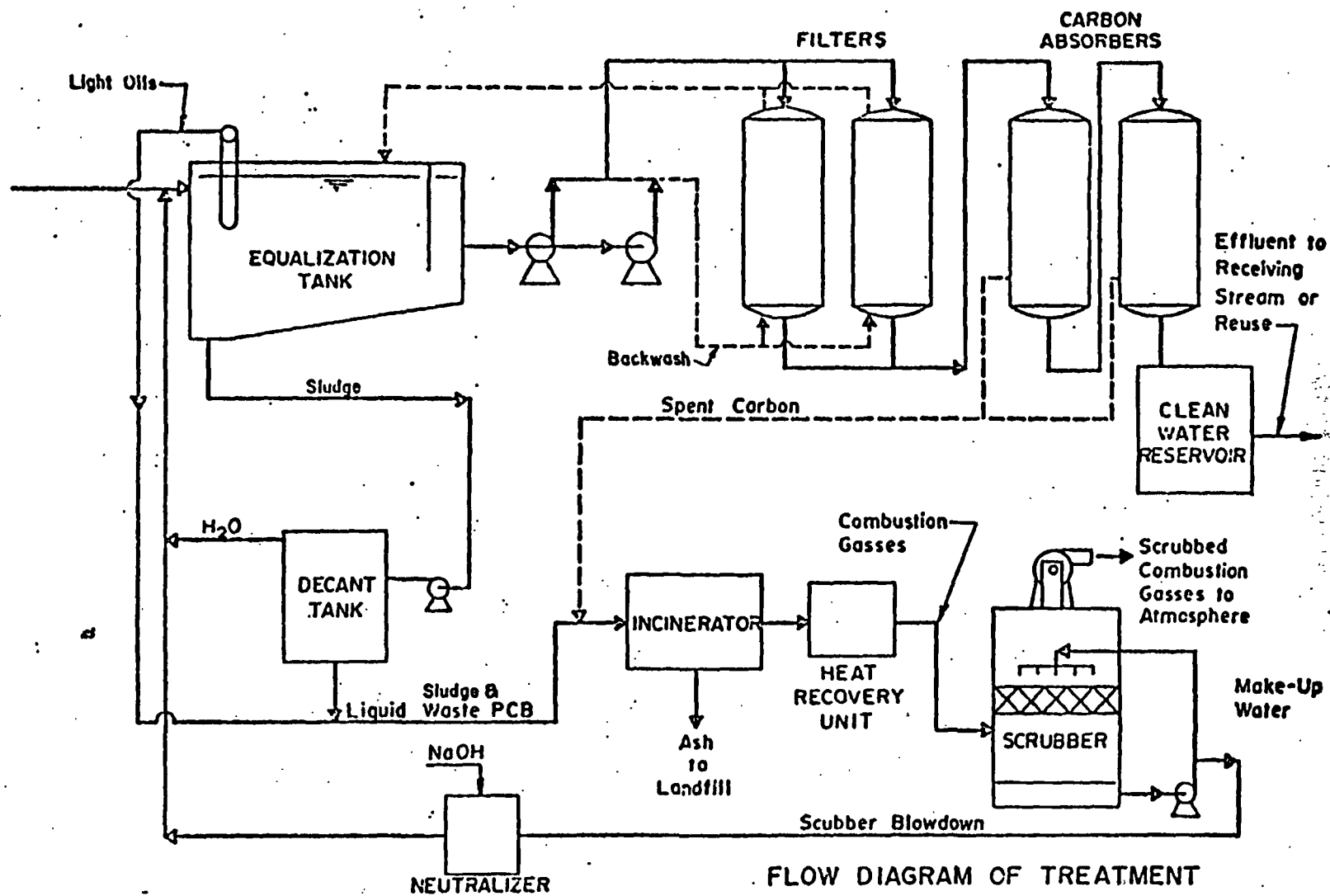


Figure 4-3. FLOW DIAGRAM OF TREATMENT SYSTEM FOR REMOVAL OF PCB FROM WASTE WATER

tion basin at an unknown concentration and leave it at 200 ppb, and that filtration will reduce the PCBs level to 50 ppb. Subsequent terminal treatment systems, i.e., carbon adsorption will reduce this PCBs concentration to 1 ppb or less. Plants which already have treatment for suspended solids and discharge less than 50 ppb of PCBs in their effluent streams may install the carbon absorption system only.

4.3 Cost References and Rationale

The basic assumptions and rationale employed in developing the wastewater treatment costs in the paper recycling industry for PCB removal can be summarized as follows:

- (1) Costs are developed for "representative plants" rather than any actual plant. "Representative plants" are defined to have a size, age, and wastewater flow agreed upon by a substantial portion of the manufacturers in this category. In the absence of such information, the arithmetic average of production size and wastewater flow for all plants is used. It should be noted that the unit costs to treat wastes at any given plant may be considerably higher or lower than the representative plant because of individual circumstances. Extrapolation of these costs to the entire industry would very likely be unrealistic.
- (2) The costs for the end-of-pipe treatment for PCBs are assumed to be essentially proportional to the volumetric flow rate of the wastewater. The treatment costs developed in the previous report⁽¹⁹⁾ for PCB removal are reassembled and presented in Figures 4-1 and 4-2.

- (3) Very limited amounts of information are available from this industry concerning the PCB concentration in the effluent and the kinds of treatment presently employed. Therefore, the estimated total annual cost for PCB wastewater treatment of a representative plant is based on the "worst case" conditions. It was assumed that "representative plants" employed no terminal treatment for PCBs removal and practiced no segregation of wastewaters containing PCBs from other in-process use waters.
- (4) Costs are developed separately for the pretreatment (equalization and multimedia filtration) and the carbon adsorption treatment of PCBs.
- (5) The capital cost is based on 8 percent interest over a period of ten years. If the supply of waste paper with substantial PCB content stops before the ten-year period is up, the capital recovery cost will increase substantially.

4.4 Cost Development

Three major categories are identified within the paper-recycling industry (see Section 4.1). The costs of wastewater treatment are developed for each individual category. Costs for pretreatment and carbon adsorption for each category are shown in Tables 4-3 through 4-5. The capital costs, operating and maintenance costs (excluding power), and power costs are taken directly from Figures 4-1 and 4-2 at given wastewater flow rates. Throughout the analysis represented by Tables 4-3 through 4-5, annual capital recovery costs were calculated based upon a ten-year lifetime and an 8 percent interest rate, consistent with the earlier reference.⁽¹⁹⁾ The capital recovery factor was thus estimated to be 0.15. All cost estimates contained in this report are based on 1976 dollars.

TABLE 4-3

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Deink Paper Manufacture

PLANT SIZE: 58,800 Metric tons of product/year

FLOW: 8,210 l/min (2,170 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	<u>Total Treatment System</u>
Invested Capital Costs:			
Total	4,600,000	860,000*	5,460,000
Annual Capital Recovery	690,000	129,000	819,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	78,000	250,000	328,000
Annual Energy and Power	58,000	17,000	75,000
Total Annual Costs	826,000	396,000	1,222,000
Cost/Metric Ton of Product	\$14.11	\$6.78	\$20.89

*Actual costing on a specific mill showed that this amount could be raised by 275% in an individual case.

TABLE 4-4

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Paperboard from Wastepaper
 PLANT SIZE: 41,800 Metric tons of product/year
 FLOW: 2400 l/min (630 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		<u>Total Treatment System</u>
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	
Invested Capital Costs:			
Total	1,500,000	260,000	1,760,000
Annual Capital Recovery	225,000	39,000	264,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	32,000	100,000	132,000
Annual Energy and Power	16,000	5,000	21,000
Total Annual Costs	273,000	144,000	417,000
Cost/Metric Ton of Product	\$6.50	\$3.43	\$9.93

TABLE 4-5

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Non-integrated Tissue Paper from Wastepaper

PLANT SIZE: 11,680 Metric tons of product/year

FLOW: 1,200 l/min (310 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	<u>Total Treatment System</u>
Invested Capital Costs:			
Total	860,000	140,000	1,000,000
Annual Capital Recovery	129,000	21,000	150,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	19,000	60,000	79,000
Annual Energy and Power	8,000	2,600	10,600
Total Annual Costs	156,000	83,600	239,600
Cost/Metric Ton of Product	\$13.36	\$7.16	\$20.52

A summary of cost estimates for PCB removal at different input PCB levels is given in Table 4-6. A summary of total capital investment cost information for PCBs from paper recycling mill effluent is given in Table 4-7. Based upon the information contained in this table, this industry, as a whole, would have to invest up to an estimated maximum of \$366,700,000 to achieve a PCB limitation of 1 ppb in their wastewaters. There is also an anticipated \$94,120,000 of annual treatment cost for the removal of PCBs from this industry. Table 4-8 is a summary of the treatment cost of PCB removal. The estimated annual treatment costs correspond to a three to five percent increase in the selling prices of products from this industry.

Depending on the amount of pretreatment required to decrease the suspended solids to a point where fouling of the charcoal beds could be avoided, costs could escalate severely. Such would be the case for effluents from deinking operations where fines loading can be heavy and particle sizes quite small.

TABLE 4-6

SUMMARY OF ESTIMATED CARBON ADSORPTION
TREATMENT COST AT DIFFERENT INPUT PCB LEVELS

<u>[PCB] Input</u> <u>(ppb)</u>	<u>Estimated Annual Carbon Adsorption Costs</u> <u>\$/kg of PCB Removed (\$/lb)</u>		
	<u>Deink</u>	<u>Paperboard</u>	<u>Tissue</u>
50	1,870 (850)	2,330 (1,060)	2,730 (1,240)
40	2,350 (1,070)	2,930 (1,330)	3,430 (1,560)
30	3,160 (1,430)	3,940 (1,800)	4,610 (2,090)
20	4,820 (2,190)	6,020 (2,730)	7,030 (3,190)
10	10,200 (4,620)	12,700 (5,770)	14,800 (6,740)
5	22,900 (10,400)	28,600 (13,000)	33,400 (15,200)

TABLE 4-7

SUMMARY OF CAPITAL INVESTMENT OF PCB
REMOVAL FROM PAPER RECYCLING INDUSTRY

	<u>Total Capital Investment in Industry,¹ Dollars</u>		
	<u>Pretreatment</u>	<u>Carbon Adsorption</u>	<u>Total</u>
Deink	78,200,000	14,600,000	92,800,000
Paperboard from wastepaper	247,500,000	6,440,000	253,900,000
Non-integrated tissue paper from wastepaper without deink	17,200,000	2,800,000	20,000,000
Total	342,900,000	23,800,000	366,700,000

¹Assume all plants in each category have production rates similar to the representative plants.

TABLE 4-8

SUMMARY OF COSTS OF PCBs REMOVAL
FROM PAPER RECYCLING INDUSTRY

<u>Category</u>	<u>Total Annual Costs (\$/kkg of product)</u>	<u>Present Selling Price (\$/kkg of product)</u>	<u>Annual Cost as percent of Selling Price</u>	<u>Total⁴ Annual Cost in Industry (\$/yr)</u>
Deink	20.89	440 - 550 ¹	3.8 - 4.7	20,900,000
Paperboard from wastepaper	9.93	220 - 330 ²	3.0 - 4.5	68,500,000
Non-integrated tissue paper from wastepaper without deinking	20.52	Not available ³	Not available ³	4,720,000 ⁵
Total				94,120,000

¹Personal communication between C.V. Fong & Mr. Zamzag - Bergstrom Paper Co.²Personal communication between C.V. Fong & Mrs. Pell - Montveill Paper Co.³Not available at the present time. Potlatch Corp. will forward this information in the future.⁴Total annual cost is obtained from multiplying total annual production by annual unit cost.⁵Assume 10% of the total U.S. tissue production is attributed to this category.

5.0 MODEL OF PCBs INVOLVEMENT IN THE PULP AND PAPER INDUSTRY

5.1 Purpose and Objectives of Model Development

Although it is generally agreed that the major input of PCBs into the paper industry has been through recycling of NCR carbonless copy paper (and this view is strongly supported by evidence presented previously in this report), there are a number of questions concerning PCBs in this industry which have not been answered:

- (1) How long will PCBs from NCR paper continue to cause significant product levels of PCBs?
- (2) How long will paper mill effluents continue to exhibit PCB levels of significance?
- (3) What are the chances for "hot spots" of PCB levels in products and effluents due to locally high concentrations of NCR paper in recycled fiber?
- (4) Are PCB levels in intake water significant at present in comparison to levels from NCR paper, with regard to product and effluent levels?

The purpose of developing and exercising a model of PCBs involvement in the paper industry was to obtain the best available answers to the above questions. By necessity, the model takes a simplistic material balance form; the major limitation of the utility and accuracy of the results obtained arises from the almost complete lack of data on process stream PCB levels and the extremely limited set of data concerning effluent and product concentrations of PCBs. However, the model does appear to be consistent with available information and does predict the PCB concentrations in various paper products and in the effluent water from paper processing plants in terms of the amount of input PCB accepted with the raw material and contained in the intake waters.

The effluent prediction is based on a constant distribution factor between the product and the effluent. Data available on sludge, effluent and products place this distribution coefficient in the vicinity of 1:1000, effluent

to product. The actual PCB concentration in the effluent entering the receiving stream will reflect the treatment process at a given site. With a more rigorous approach to the distribution coefficient, one would be able to narrow the limits of predictability considerably. We have aimed at the center of the array in order to maintain a tie to "average" conditions.

At all times it is realized that the model is only a general one; no attempt has been made to apply it to a particular mill. A simple mass balance calculation with known PCB inputs, water flows and production outputs would be a straightforward task for a given site.

The model does show that a mill which accepts NCR carbonless copy or converter scrap, has poor suspended solids removal and has a high PCB level in its intake water might be capable of producing a high PCB effluent as a local "hot spot". Present values for recycled wastepaper⁽⁶⁾ indicate this likelihood to be continually decreasing. However, the expected frequency or severity of hot spots cannot be fully addressed because of lack of data.

5.2 First Order Model of Paper Industry

5.2.1 Assumptions

The model is based upon the following assumptions:

- 1) The two primary sources of PCB to the paper industry are:
 - a) NCR carbonless copy paper made between 1957 and 1971 and its associated converter scrap at 3.4% PCBs by weight; and
 - b) The PCB load of the intake waters, taken to average 0.1 ppb.
- 2) A secondary source is PCBs already existing in recycled paper due to 1a and 1b above.
- 3) The routes of PCBs out of the paper industry are limited to:

- a) Product
 - b) Effluent
 - c) Sludge and other solid wastes (or process loss)
 - d) Evaporation
- 4) Most of the PCBs in the paper industry remain associated with the fiber, either as product or as sludge. This appears to be due to the presence of PCBs in microspheres used in the NCR paper plus the low solubility of PCBs in aqueous solution and its preferential association with surfaces and organic rich interfaces. In some cases PCBs found in industrial effluents are almost quantitatively associated with the suspended solids.
- 5) Evaporative losses of PCB will depend to a great deal on the integrity of the capsular form. Industry experts have been quite unanimous in their agreement that capsular breakage would be small. The evaporative losses intimated by some of the mass balances attempted at the Institute of Paper Chemistry are very small compared to the amounts of PCB moving through the systems. As a result, we have chosen to neglect evaporative losses in the treatment of the model since any assessment would be fragmentary at best.
- 6) Contributions of PCB by inks or adhesives are negligible and not considered to be large enough to affect even a locale distribution. Based on the estimation presented in Section 3.1, the upper bound of PCBs into paper products other than the NCR paper appears to be on the order of 50,000 to 100,000 pounds, much less than one percent of the total PCBs usage in the NCR paper during the same time frame. Thus, non-NCR PCBs should be negligible with regard to the model.

- 7) Prior to 1957, when NCR carbonless copy paper was introduced, the PCB content of paper products would have been controlled by the PCBs carried with the intake water. The effluent would have been cleaned by the passage of PCBs from the water to the fiber during the pulping and paper making process. Total transfer for a typical process would have produced a paper with a PCB concentration of 0.02 ppm. Based on this consideration, and the realization that present day detection limits for PCB in paper are in the vicinity of 0.1 ppm, the model has been exercised neglecting the intake water contribution.
- 8) The two routes for PCB return on NCR paper are:
- a) As part of the recycling waste paper stream in "mixed" or deinked grades of paper stock.
 - b) As converter scrap purchased by mills that use it as furnish (raw material).

Other assumptions or specific decisions made in developing the model will be indicated at the point where the information is used or the equation described.

5.2.2 Model Structure

The first order model is an overview of the industry as a whole. Mass balance considerations are utilized to develop a "one-box" representation. Such a treatment avoids the complexity of the actual recycling web, and applies the limited data on PCB concentrations of waters, product and sludge to produce a first look at the time rate of change of PCB levels in average product as a result of the growth and eventual cessation of NCR carbonless copy paper in the recycled waste stream. This admittedly simple approach serves as a foundation upon which to further divide the industry, as well as providing a qualitative validation of many of the accepted descriptions of PCB occurrence within the industry.

Figure 5-1 shows a schematic representation of the first order paper industry model, where:

- $E(t)$ - evaporative losses of PCB. These losses are yet to be assessed on an industry wide scale, but early indications are that they are not dramatic. Any such losses would have the effect of lowering product, effluent and sludge PCB concentrations, but would not change the relationship between these.
- $V(t)$ - input of virgin wood pulp. Virgin wood has been found to be relatively free of PCBs, but may pick up some from the water used in the pulping stages.
- $W_{in}(t)$ - intake water. Census Bureau data for total water usage are relied on. The typical intake water PCB concentration is taken to be 0.1 ppb. This value is probably an upper bound on a natural water and nonetheless turns out to have only a small effect on PCB concentrations found in the paper industry.
- $S(t)$ - sludge output. This is the amount of process loss going to sludge. It is inferred that sludge output is proportional to the production rate and has the same concentration of PCBs as the product.
- $R(t)$ - amount of paper stock being recycled. The average lifetime of paper products is taken to be 1 year before recycling. Hence the concentration of PCBs in the paper stock is assumed to be that of the previous year's product.
- $W_{out}(t)$ - effluent water. It is generally held that PCBs in the effluent are strongly associated with the suspended solids. In the present case the effluent can be considered what might typically remain after primary treatment, removal of settleable solids and some suspended solids. How much removal occurs in an actual mill will depend on the type and amount of treatment available. It has been assumed here that the effluent PCB concentration is proportional to the product concentration. The constant of proportionality would depend on the treatment system efficiency for solids removal. But in

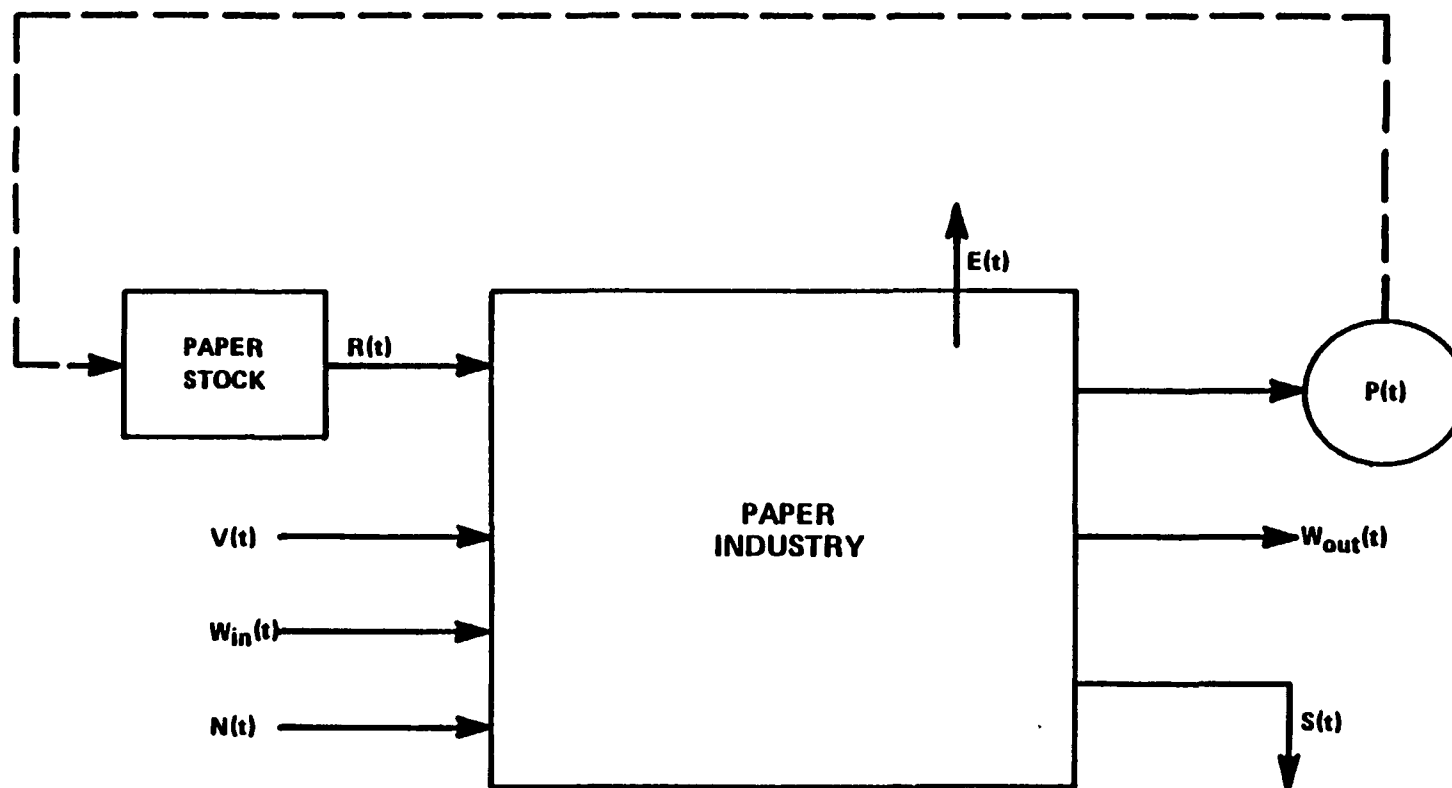


Figure 5-1. SCHEMATIC OF FIRST ORDER MODEL OF PAPER INDUSTRY

any case, the effluent concentration predicted by the model gives an idea of the PCB which might escape into the environment without further consideration and treatment.

- P(t) - annual production of the industry.
- N(t) - PCBs introduced to the paper industry as a result of NCR carbonless copy converter scrap and recycled used sheets. While NCR production figures for carbonless copy paper and its PCB content are known, the amount recycled from office and other commercial institutions or from converting operations can only be guessed at. Converter scrap varies between 10 and 15% (15% was the figure used in an A.D. Little Paper Industry study) for printing and writing grades.⁽²⁰⁾ However, much of this scrap was recycled in-plant, back into NCR carbonless forms - this amount could not be estimated by personnel at Mead (the manufacturers for NCR). Shade Information Systems, Inc., a converter of carbonless and a supplier of post-consumer office waste, in testimony before the Department of Natural Resources in Wisconsin, estimated that 10% of all office waste is presently recycled, that of this recycled paper, 10% came from old files and 90% from yearly usage, and that the average lifetime for files is three years.⁽²¹⁾

According to Mr. Ed Nastar of the International Business Forms Association, the major uses for carbonless paper are in invoices and customer statements with tax forms using a lesser amount. If one extends the Shade estimates to include commercial establishments like stores with offices then one can use the same estimates for carbonless paper: 10% of each years production is eventually recovered with 90% of that recovered coming from the previous year and the other 10% coming from old files with a three year half life. These estimates are used in the model. (To show the sensitivity of the model to the NCR recovery rate a 20% figure will be presented). Table 5-1 shows NCR production from 1957-1971.

Table 5-1
PCB Used in Carbonless Copy Paper

<u>Year</u>	<u>PCB in NCR Paper Manufactured (10⁶ Pounds)</u>
1957	58.7
1958	77.9
1959	101.9
1960	114.9
1961	164.3
1962	195.3
1963	228.1
1964	270.5
1965	348.9
1966	424.6
1967	435.5
1968	580.1
1969	627.8
1970	661.1
1971	126.6
1972	0
1973	0
1974	0
1975	0

Since the amount of old NCR carbonless recycled into the industry can only be estimated and few measurements on other than recycled box-board exist by which to validate the figures, the exact levels predicted by the model should be regarded with caution. Nonetheless, the model does reflect the trends and dynamics of PCB involvement in the industry.

The PCB mass balance equation for the First Order Model is written:

$$R(t)C_p(t-1) + N(t) + W_{in}(t)C_{w_{in}}(t) = P(t)C_p(t) + S(t)C_p(t) + W_{out}(t)C_{w_{out}}(t)$$

where:

- $C_p(t)$ \equiv PCBs concentration in product for year t .
- $C_{w_{in}}$ \equiv PCBs concentration in input water (taken to be 0.1 ppb)
- $C_{w_{out}}(t)$ \equiv PCBs concentration in effluent $\equiv \lambda C_p(t)$ where λ is a constant dependent on the level of suspended solids.

In EPA data (1, p. 84) the suspended solids are shown to range from 500 ppm in non-deinked paper mills to 1700 ppm in deinking effluents. Considering that the best available technology is not uniformly used now or in the past, 1000 ppm is assumed for a suspended solids load, and the model is exercised with λ at $\frac{1}{1000}$. From John Strange Paper Co. data a λ of $\frac{2}{1000}$ was obtained while Ft. Howard information indicated λ at $\frac{1.1}{1000}$ to $\frac{1.2}{1000}$.

and: $S(t)$, the sludge output is taken to be proportional to $P(t)$. That is:

$S(t) = \xi(t)$, where ξ is the proportionality constant.

A value of 4.5% was chosen for ξ , based on previously reported data for process losses. (22)

Rewriting the previous equation,

$$R(t)C_p(t-1) + N(t) + 10^{-10}W_{in}(t) = C_p(t) \left[\underbrace{0.955}_{1-\xi} P(t) + \underbrace{10^{-3}}_{\lambda} W_{out}(t) \right]$$

As a simplistic first exercise - assume $\lambda = 0$, i.e., all PCB is retained by the product. Let the $N(t)$ assume three cases:

A_I - 10% recovery

A_{II} - 15% recovery (10% recycle + 5% converter scrap)

A_{III} - 25% recovery (20% recycle + 5% converter scrap)

Figure 5-2 shows the PCB concentration in the product for these three different recovery rates. The NCR production is also plotted as a reference to show the roll-off of the curves.

Immediately obvious is the direct and quantitative relation between the NCR recovery and PCBs in the product. Product levels rapidly fall below the 1 ppm level by 1973 or 1974, so that input water concentrations ($W_{in}(t)$) appear to be completely dominated by the NCR contribution.

Further insight is gained if the data of A_{II} (15% recovery) are plotted again with $R(t) = \text{zero}$; that is, if there was no recycling of product back into the paper stock input. Figure 5-3 shows the result of this exercise. For the overall industry under these conditions, 15% NCR recovery appears to be responsible for about 83% of the PCB in the product. However, if broken down further, specific segments of the industry which utilize a large proportion of wastepaper in their furnish would be expected to exhibit a larger dependence on the PCBs recycling to the paper stock input.

The effect of process loss to sludge is easily demonstrated in a tabular format. Table 5-2 shows the 15% NCR recovery data now allowing $R(t)$ to operate (i.e., recycling to paper stock) and λ values of 0 (plotted in Figure 5-2), 10^{-3} , and 2×10^{-3} . According to the data on Table 5-2, a λ of 10^{-3} (ratio of PCBs level in effluent to TSS level in effluent) decreases the PCBs levels in the product by only about ten percent from those at zero PCBs in the effluent ($\lambda = 0$). A further reduction of six to ten per cent in product PCB levels results from application of $\lambda = 2 \times 10^{-3}$. As further internal reuse schemes for white water proliferate a continuing decrease would be expected in both suspended solids and λ . All peripheral factors point to a continuing association of the majority of PCBs introduced into the system with the product.

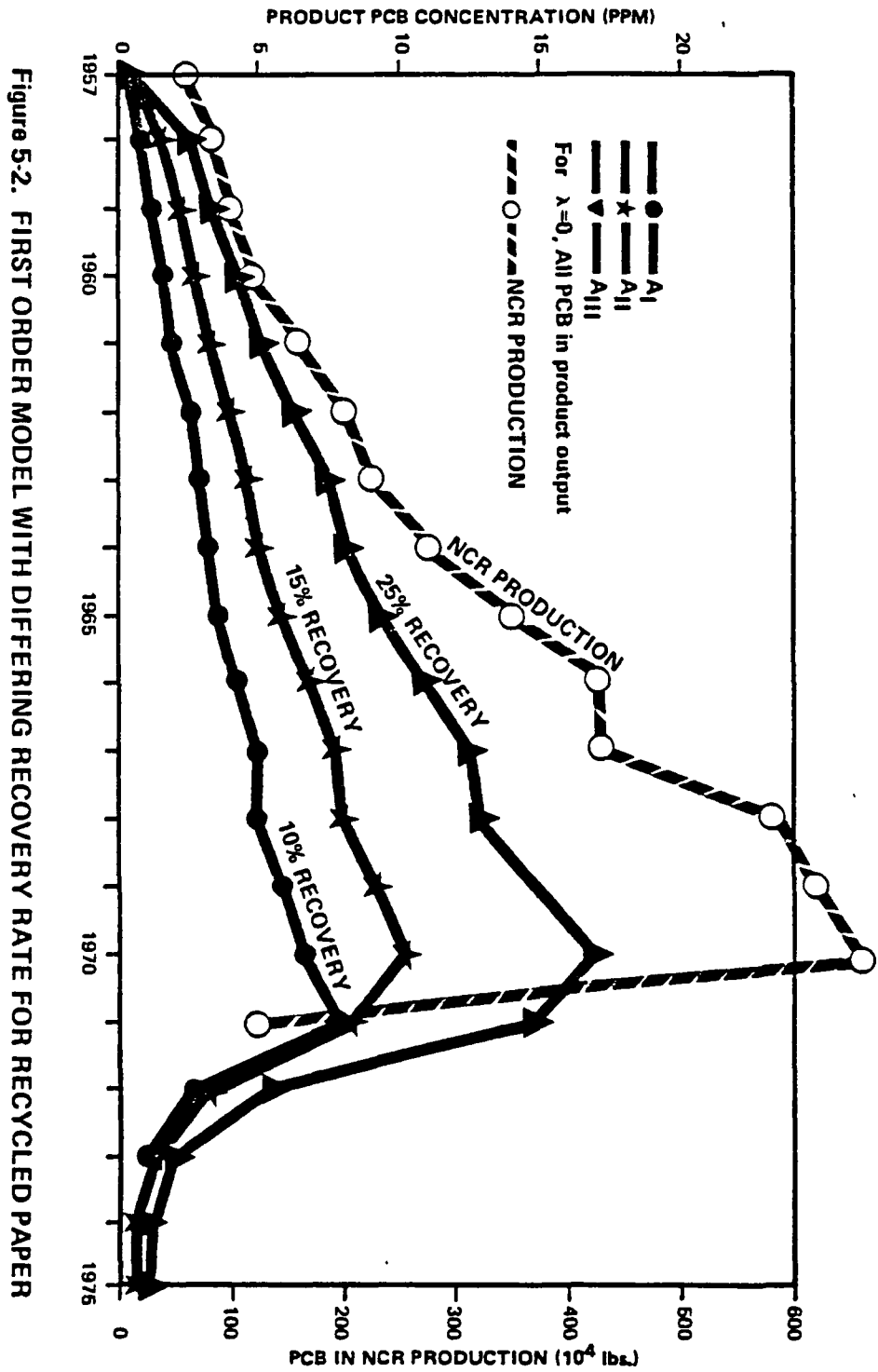


Figure 5-2. FIRST ORDER MODEL WITH DIFFERING RECOVERY RATE FOR RECYCLED PAPER

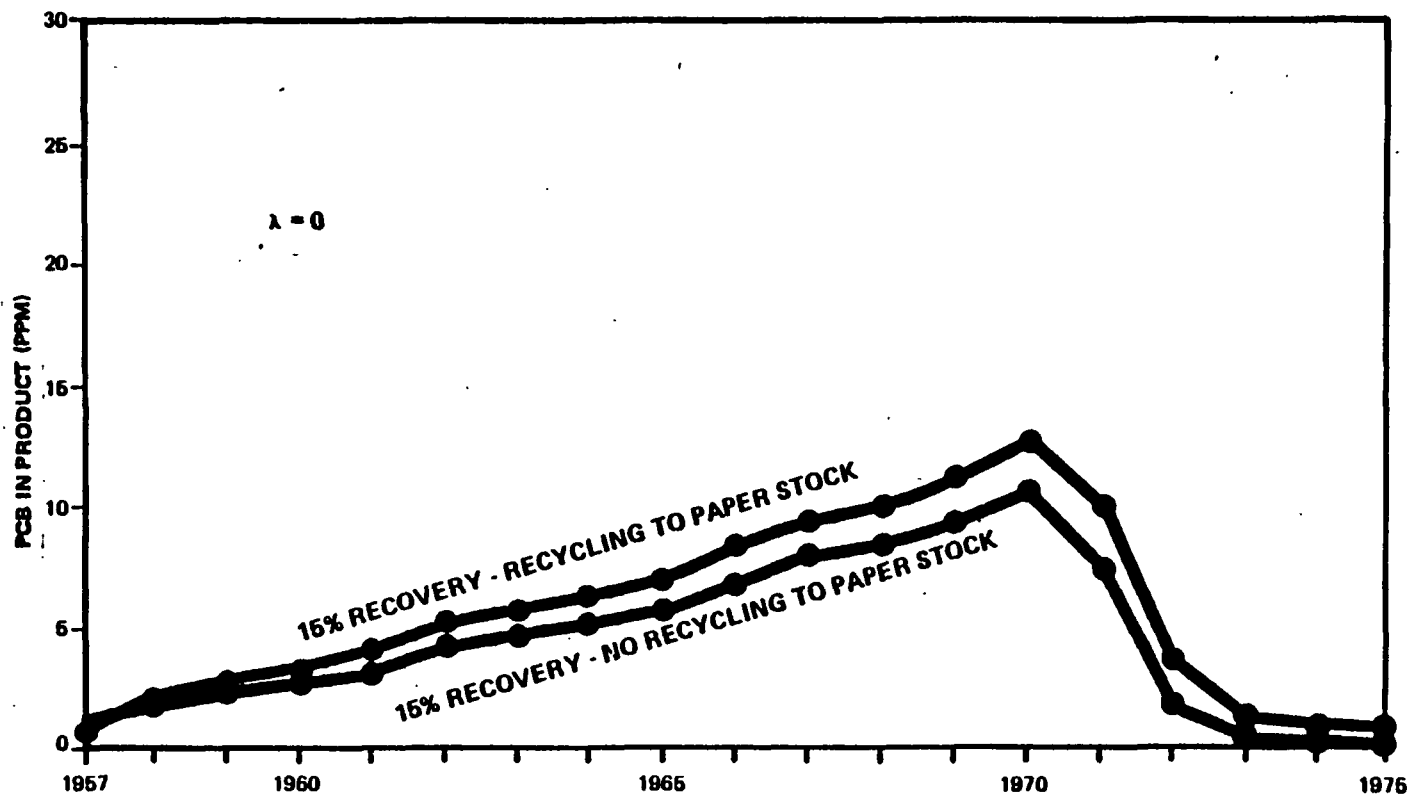


Figure 5-3. AFFECT OF RECYCLING PAPER OTHER THAN NCR CARBONLESS PAPER ON PCB CONTENT OF FIRST ORDER MODEL PRODUCTION

Table 5-2

PCB Concentration in Product (ppm)

<u>Year</u>	<u>$\lambda=0$</u>	<u>$\lambda=10^{-3}$</u>	<u>$\lambda=2 \times 10^{-3}$</u>
1957	0.48	0.43	0.39
1958	1.58	1.41	1.27
1959	2.15	1.93	1.75
1960	2.66	2.39	2.16
1961	3.20	2.88	2.62
1962	3.96	3.58	3.26
1963	4.58	4.15	3.79
1964	5.04	4.59	4.20
1965	5.68	5.28	4.85
1966	6.76	6.21	5.72
1967	7.69	7.04	6.49
1968	8.08	7.42	6.86
1969	9.18	8.46	7.85
1970	10.20	9.40	8.72
1971	8.03	7.40	6.86
1972	2.83	2.61	2.43
1973	0.86	0.80	0.74
1974	0.45	0.42	0.39
1975	0.33	0.30	0.28

This general overall look at PCBs demonstrated the following:

- a) A 1970-71 peak in product PCB concentrations corresponding to maximum PCB usage in NCR paper plus a one-year or less delay in reaching maximum PCB levels in the recycling stream.
- b) With the cessation of NCR production the drop off in product PCB was rapid. Different specific industry segments would show a different drop off rate (this is investigated with the second order model).
- c) Using reasonable choices for the adjustable constants, the major source of PCB is the NCR carbonless paper's direct input to the industry. Further recycling of paper contaminated by recycled NCR input has a relatively small effect on the concentration observed in the paper product.
- d) It is difficult to assess the quantitative effects of such industry responses to the PCBs problem as elimination of deinking grades as furnish for food board. There is no doubt that within a specific segment of the industry such activity was beneficial. In the overview of the first order model, however, these effects cannot be separated out. The model as developed exhibits an overwhelming response to the NCR carbonless recovery rate which would inundate any analysis of a finer internal structure.

5.3. Second Order Model of Paper Industry

5.3.1 Industry Categorization for Second Order Model

The obvious industry categorization useful to a more detailed industry analysis is paperboard; paper; and construction paper and board. The latter segment includes portions which use 100% recycled paper stock (construction paper) and others which use little, if any, recycled paper stock (construction board) and can be further subdivided on this basis. Figure 5-4 shows schematically

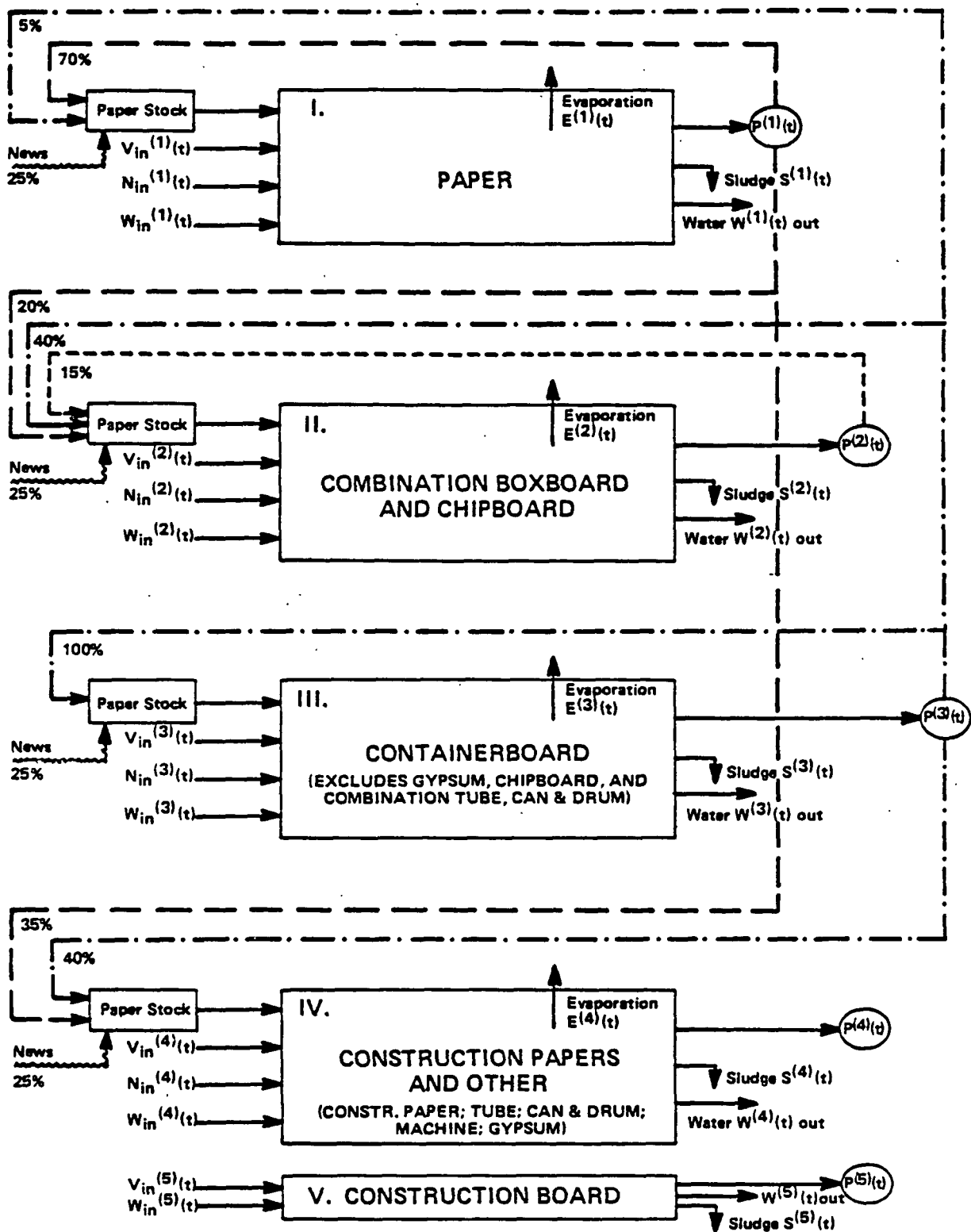


Figure 5-4. SCHEMATIC OF SECOND ORDER MODEL

the five categories selected and the flows of products returning to these industry segments in recycled waste streams as well as other inputs, products, and discharges. Figure 5-4 is thus essentially a schematic diagram of the second order model. Annual production data from 1957 through 1974 for each of the five industry segments are presented on Table 5-3.

Segment I, paper, has a product output approximately equal to the sum of segments II, III, and IV. This should be remembered when one assesses the total load of PCB associated with the production of a given segment. The load will be PCB concentration times the output.

Segment II, combination boxboard and chipboard, is based on a raw material which is 100% recycled. Historical PCB data (back to 1971) exists for combination boxboard. Almost all of the deinked paper stock (ledger grades) went into box production prior to 1971; also, most of the mixed grades and pulp substitutes went into box production. As a result, most NCR paper entering the general area of paperboard would probably wind up associated with combination boxboard and chipboard. Chipboard is included since sufficient data were available on this category, ⁽²³⁾ but chipboard is less than 10% of this segment's total output.

Segment III contains those items which are primarily made from virgin wood or recycled product from Segment III.

Segment V, construction board, uses all virgin wood and is not recycled.

Segment IV is a composite segment, the components of which have the following characteristics:

- a) All use a high percentage of mixed waste which could contain NCR sheets.
- b) Many products are used in building applications which precludes their entry into the recycled waste stream.
- c) The tube, can and drum component is not likely to be recycled, though it has an open usage different than the building materials.

Table 5-3
Annual Production for Industry Segments (10⁶ tons)

<u>Year</u>	<u>I</u> <u>Paper</u>	<u>II</u> <u>Combination</u> <u>Boxboard</u> <u>&</u> <u>Chipboard</u>	<u>III</u> <u>Containerboard</u>	<u>IV</u> <u>Construction</u> <u>Papers and</u> <u>Others</u>
1957	13.6	3.9	8.9	2.7
1958	13.5	4.0	8.8	2.8
1959	15.0	4.2	9.8	3.1
1960	15.4	4.2	10.3	2.8
1961	15.7	4.3	10.9	3.0
1962	16.5	4.3	11.6	3.1
1963	17.3	4.4	12.2	3.2
1964	18.2	4.5	13.4	3.4
1965	19.2	4.7	14.4	3.5
1966	20.7	5.0	15.9	3.3
1967	20.9	4.1	16.5	3.1
1968	22.4	4.4	18.4	3.5
1969	23.6	4.3	20.0	3.5
1970	23.6	4.1	19.7	3.5
1971	23.8	3.8	20.3	4.0
1972	25.4	3.9	22.4	4.3
1973	26.5	4.0	23.3	4.3
1974	26.9	3.5	22.2	4.2

5.3.2 Equations

The same definitions of mathematical terms hold for the second order model as for the first order model (see Sec. 5.2.2), applied on a segment-by-segment basis. In addition, the second order model uses superscripts to denote association with a particular industry segment. Other symbols used are:

$C_v^{(1)}(t) \equiv$ PCB concentration of virgin wood in industry segment 1.

$C_e^{(1)}(t) \equiv$ PCB concentration in aqueous solution of effluent from segment 1.

The following are based on our assumptions:

$$C_v^{(1)}(t) = C_v^{(2)}(t) = C_v^{(3)}(t) = C_v^{(4)}(t) = C_v^{(5)}(t) \equiv 0$$

$$C_{win}^{(1)}(t) = C_{win}^{(2)}(t) = C_{win}^{(3)}(t) = C_{win}^{(4)}(t) = C_{win}^{(5)}(t) \equiv 0$$

$$E^{(1)}(t) = E^{(2)}(t) = E^{(3)}(t) = E^{(4)}(t) = E^{(5)}(t) \equiv 0$$

and,

$$\left. \begin{aligned} C_{wout}^{(1)}(t) &\equiv \lambda_1 C^{(1)}(t) \\ C_{wout}^{(2)}(t) &\equiv \lambda_2 C^{(2)}(t) \\ C_{wout}^{(3)}(t) &\equiv \lambda_3 C^{(3)}(t) \\ C_{wout}^{(4)}(t) &\equiv \lambda_4 C^{(4)}(t) \\ C_{wout}^{(5)}(t) &\equiv \lambda_5 C^{(5)}(t) \end{aligned} \right\} \quad \text{where } \lambda\text{'s are constants.}$$

Since newsprint contains little if any PCB,

$$N^{(3)}(t) \equiv 0$$

$$N^{(5)}(t) \equiv 0$$

Prior to 1957,

$$C_p^{(1)}(t) = C_p^{(2)}(t) = C_p^{(3)}(t) = C_p^{(4)}(t) = C_p^{(5)}(t) \equiv 0$$

After 1957 one has these 5 unknowns, and the following 5 equations:

$$(1) \quad N^{(1)}(t) + \left[.70R^{(1)}(t)C_p^{(1)}(t-1) + 0.05R^{(1)}(t)C_p^{(3)}(t-1) + .25R^{(1)}(t)(0) \right] \\ = \left[P^{(1)}(t) + S^{(1)}(t) + \lambda_1 W_{out}^{(1)}(t) \right] C_p^{(1)}(t)$$

$$(2) \quad N^{(2)}(t) + \left[0.15R^{(2)}(t)C_p^{(2)}(t-1) + 0.20R^{(2)}(t)C_p^{(1)}(t-1) + \right. \\ \left. 0.40R^{(2)}(t)C_p^{(3)}(t-1) + 0.25R^{(2)}(t)(0) \right] \\ = \left[P^{(2)}(t) + S^{(2)}(t) + \lambda_2 W_{out}^{(2)}(t) \right] C_p^{(2)}(t)$$

(This holds until 1971 at which time the paperboard segment greatly decreased their usage of recycled paper. Thus, the coefficient of 0.20 for the paper portion of the paper stock input is taken to be zero for years after 1971.)

$$(3) \quad \left[R^{(3)}(t)C_p^{(3)}(t-1) \right] = \left[P^{(3)}(t) + S^{(3)}(t) + \lambda_3 W_{out}^{(3)}(t) \right] C_p^{(3)}(t)$$

$$(4) \quad N^{(4)}(t) + \left[0.35R^{(4)}(t)C_p^{(1)}(t-1) + 0.40R^{(4)}(t)C_p^{(3)}(t-1) + 0.25R^{(4)}(t)(0) \right] \\ = \left[P^{(4)}(t) + S^{(4)}(t) + \lambda_4 W_{out}^{(4)}(t) \right] C_p^{(4)}(t)$$

$$(5) \quad 0 = \left[P^{(5)}(t) + S^{(5)}(t) + \lambda_5 W_{out}^{(5)}(t) \right] C_p^{(5)}(t)$$

Notes:

- (a) From equation (5) $C_p^{(5)}(t) = 0$ for all (t) .
- (b) From equation (3) $C_p^{(3)}(t) = 0$ for all (t) .
- (c) All λ 's are from .001 to .002. This allows us to ignore λ terms since they are so much smaller than the $P(t)$ and $S(t)$ terms.

Substitution yields:

From equation (1)

$$N^{(1)}(t) - 0.70C_p^{(1)}(t-1)R^{(1)}(t) = [P^{(1)}(t) + S^{(1)}(t)]C_p^{(1)}(t)$$

From equation (2)

$$N^{(2)}(t) + [0.20C_p^{(1)}(t-1) + 0.15C_p^{(2)}(t-1)]R^{(2)}(t) = [P^{(2)}(t) + S^{(2)}(t)]C_p^{(2)}(t)$$

(The 0.20 constant drops to 0 after 1971 as noted above)

From equation (4)

$$N^{(4)}(t) + 0.35R^{(4)}(t)C_p^{(1)}(t-1) = [P^{(4)}(t) + S^{(4)}(t)]C_p^{(4)}(t)$$

Equations (3) and (5) are negligible, based on Notes (a) and (b) above.

5.3.3 Quantitation and Exercise of the 2nd Order Model

McLenahan's study of 1969-1970 paper stock usage was used as the basis for quantitating the model.⁽²³⁾ This extensive study accounted for over 90% of the wastepaper stock usage. It also tabulated the paper stock by type and associated that with its end use. A number of other studies have since been based on these figures; utilization of these data thus keeps the model on a somewhat parallel footing for comparison with the other studies.

The second order model is a good deal more complex than its predecessor in Section 5.2. To explore the effects of recycling on specific segments of the industry it was necessary to subdivide the industry into identifiable sectors. This necessitated developing a reasonable set of criteria for routing the recycled paper between these sectors.

The following additional assumptions were made:

- 1) Paper products produced one year are considered to be recycled the next.
- 2) The paper stock percentages of various inputs were taken to be constant over the period 1957 to 1974, except in the combination boxboard and chipboard category after 1970. In this category, industry reaction to PCB in food packaging and the eventual FDA 10 ppm limit is reflected.
- 3) Each segment's percentage of the overall paper stock usage is constant from 1957 to 1974 using the 1969 percentage. The model is quite insensitive to changes in this parameter.
- 4) Recycled newsprint is considered to be PCB free. Newsprint is produced primarily from virgin fiber, and the only paper stock used in newsprint is other newsprint. Consequently, no PCB from NCR paper should be introduced into this segment. Measurements by Hazleton Laboratories in 1972 confirm low background values of PCBs in newsprint.⁽⁹⁾

Since newsprint is only a small percentage of paper output it was not set aside as a separate category. However, newsprint is a sizeable fraction of the recycled waste stream and here it was accounted for separately.

- 5) Containerboard uses very little paper stock, and what it does use is old containers or container clippings. (This excludes gypsumboard, chipboard, and recycled tube, can and drum segments). We therefore approximated paper stock in this subcategory to be 100% container. This implies that containerboard will be PCB free.
- 6) As before, process loss to sludge was assumed to have the same PCB concentration as the product. The process loss estimates are those previously published for 1970.⁽²²⁾
- 7) Bureau of Census data was used to obtain values for total paper stock recycled.
- 8) The model is very sensitive to the total amount of NCR carbonless copy paper recycled into the industry, and to its distribution within the industry. Uncertainties in these affect the details of the model, but not the general trends.

- 9) Virgin wood contains negligible PCB.
- 10) PCB concentration of input waters is taken to be 0.1 ppb.
- 11) Evaporative losses are not considered for the reasons given for the first order model exercise in Section 5.2.
- 12) The "mixed" category of waste paper includes #1 and #2 mixed, super mixed, boxboard clippings and mill wrappers. The amounts of each going into "mixed" in 1969 was investigated by other workers. (20,23) Paper stock dealers interviewed indicated that "mixed" paper was usually office waste with the following approximate composition:

	<u>Range (%)</u>	<u>Chosen for Model</u>
Old Corrugated Cartons	0-15	10
Newsprint	10-25	20
High-Grade Printing & Writing	60-90	70

- 13) The loss of PCBs in solution in effluent waters is assumed to be negligible compared to PCBs associated with the suspended solids.

The model is exercised for two distribution schemes for NCR paper as follows:

- a) The NCR received in a given year is assumed to be 5% of the converter scrap from that year's production and 10% of the post consumer wastepaper. Of the post consumer waste 9/10 came from the previous production year and 1/10 came from years prior to that.

(A three year half-life with exponential decay is postulated for the post consumer waste NCR paper which is recycled more than 1 year after being produced. This assumption is significant only after 1971.)

All of the 5% NCR converter scrap is assumed to go into the paper segment of the industry. The combination boxboard segment rejected it due to a discoloration problem.

The recovered post consumer NCR was distributed according to the percentage of printing and writing paper being recycled within each segment. 70% of

the mixed category was taken to be printing and writing paper except within boxboard paper stock where it is estimated that 50% of the mixed was actually boxboard clippings. About 2/3 of the deinking category is taken to be printing and writing paper. The final breakdown of NCR in the paper stock for each segment thus becomes:

PAPER - 5% converter scrap

3% post consumer

COMBINATION BOXBOARD AND CHIPBOARD - 3.5% post consumer

CONSTRUCTION PAPER - 3.5% post consumer

After 1970 the combination boxboard segment drastically reduced the use of ledger grade papers and some pulp substitutes. This was industry's response to eliminate NCR from inadvertently contaminating the foodboard grades. In the model, the NCR entry figures for that segment are adjusted to reflect this industry action. The NCR going into the paper segment may have increased its percentage of NCR received as a result. Though this is not entirely clear, it has been included in the second exercise of the model.

Figure 5-5 shows the response of the model. The rapid decrease in segment II PCB levels after 1970 is evident. Concomitant reductions occur in segments I and IV. While the latter two reflect the loss of the NCR carbonless copy paper production, the former shows cessation of PCBs usage by NCR as well as additional reduction caused by the industry action.

A second exercise of the model, shown on Figure 5-6, is made on the assumption that 10% of the returning NCR is sent to the paper and boxboard segments based on the use of deinking stock. The paper segment has not used mixed grades and boxboard officials state that their product has not used mixed grades, although several references indicate some usage.^(20,23) The second exercise is performed with the assumption that the boxboard segment (II) does not use mixed grades, other than boxboard clippings.

10% recovery of wastepaper is calculated at 9% the year after production, and 1% thereafter based on the 3 year half-life described earlier.

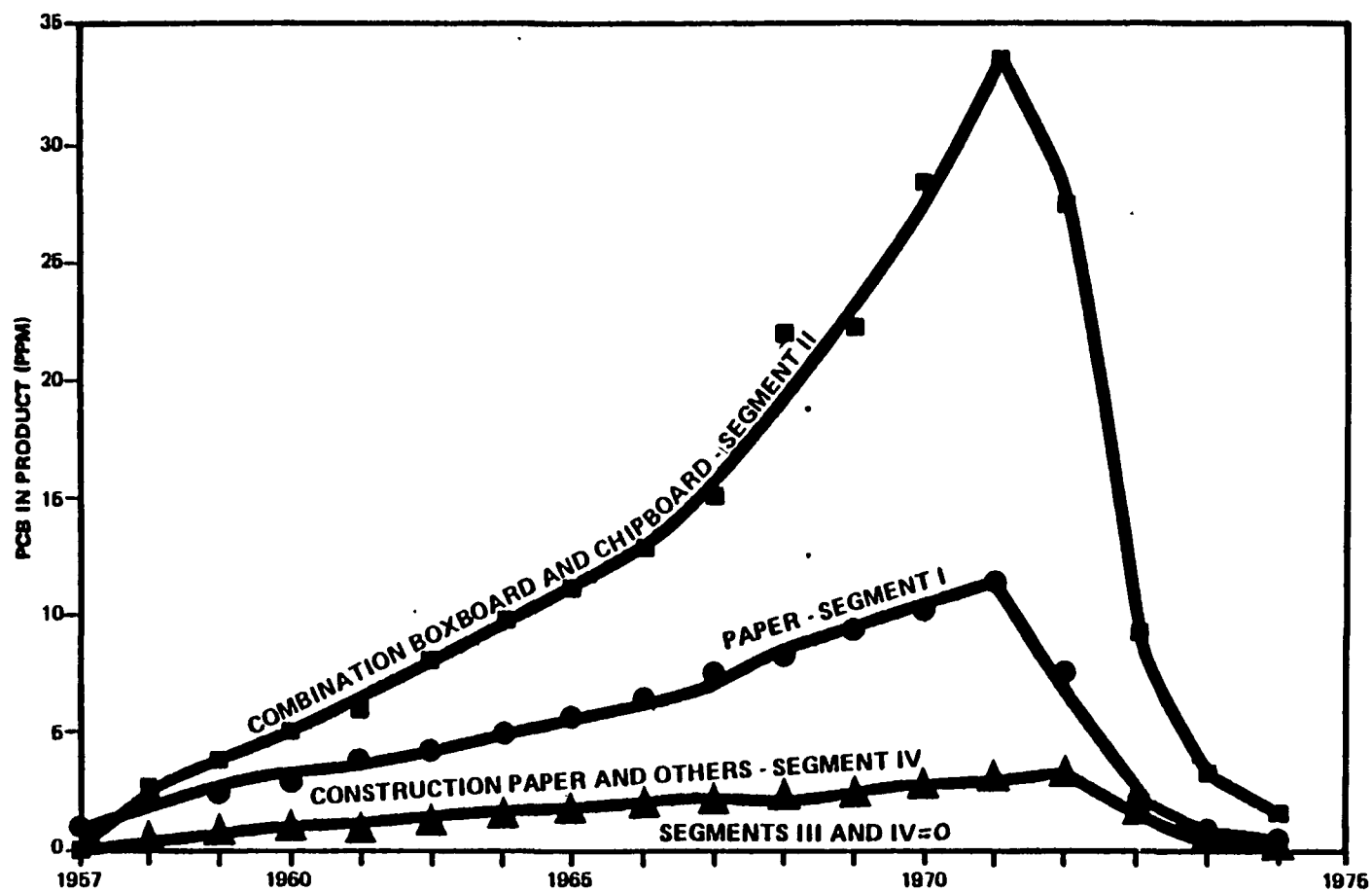


Figure 5-5. FIRST EXERCISE OF SECOND ORDER MODEL

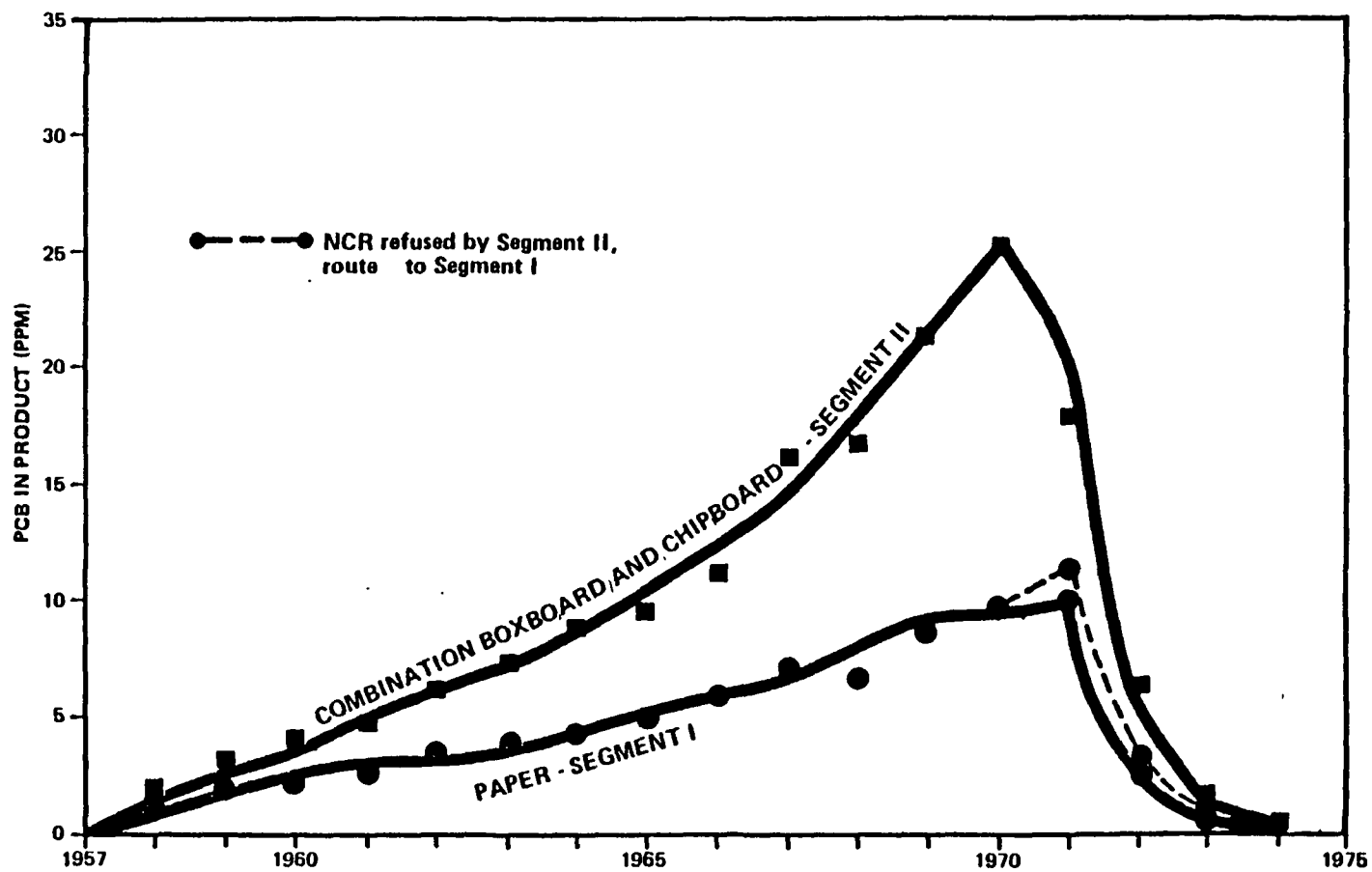


Figure 5-6. SECOND EXERCISE BY SECOND ORDER MODEL

The post-1970 reduction of NCR into the combination boxboard segment is included. The reduction in ledger grade usage by boxboard is assumed to have been by half in 1971 and complete stoppage thereafter. If the ledger stream might have diverted to the paper segment upon its rejection by the boxboard (segment II), the effect this would have had on the paper PCB is shown by a dotted plot from 1971 on in Figure 5-6.

Overall, we see the same general trends in both exercises (Figures 5-5 and 5-6). The routing chosen for the returning PCB in the NCR paper effects the details of the product concentrations, as does the relative size of the production output within each segment.

In each scenario, the primary removal of PCB containing NCR from production allowed a return of every segment to pre-1957 PCB levels in the products by 1974 or 1975. This trend is reflected in the decreases shown by available data in Table 3-2. The decreases documented are of the same general magnitude as produced by the model. Data on "recycled wastepaper input" (6) has reflected a drop to 0.15 ppm in 1976, which is near the detection limit of the analysis for PCB in paper products.

5.4 Discussion of Model Results

The results obtained from exercising the model show clearly the overwhelming dependence of PCB levels in both product and effluents upon the NCR paper content of recycled fiber. According to these results, product levels of PCBs resulting from the NCR paper should be less than one ppm by the present time (1976) with the possible exception of the combination boxboard and boxboard segment, and of course, excepting localized hot spots caused by inclusion of small amounts of NCR paper in the fiber recovery stream. This result agrees with recent analytical results on PCB levels in paper industry products. Product levels, effluent levels, and frequency and severity of hot spots should continue to decline slowly as the PCBs in paper products are diluted further with virgin and less contaminated secondary fiber.

The ratio of PCBs concentration to TSS in the effluents had little effect on product levels, as would be expected. Values of this ratio in the range of

0.001 to 0.002 appear to be consistent with available data on both effluents and products. This result indicates that most of the PCBs entering the process exit in the product and thus generally agrees with the analysis of Section 3.

The overall agreement of the results obtained with the model tend to support the various assumptions made. Agreement is reflected by comparison with available data on both product and effluent PCB levels. Thus, the model as presented does appear to represent a reasonable and consistent material balance for PCBs around the paper industry.

A distribution for incoming PCBs between product, effluent, and waste treatment sludge can be calculated based on the results of the model. Using the following values:

- (1) PCBs level on product = 1 ppm of solids
- (2) PCBs on solids in wastes = 2 ppm of solids
- (3) 90 percent removal of solids and PCBs in wastewater treatment
- (4) 135 ppm suspended solids in final effluent
- (5) 0.27 ppb PCBs in final effluent
- (6) Zero loss through vaporization

The results obtained are:

<u>Plant Stream</u>	<u>Percentage of Incoming PCBs Contained Therein</u>	<u>Weight of Stream*</u>	<u>PCBs Level in Stream</u>	<u>Solids Content</u>
Product	75-80	1 kkg	1 ppm	95-96%
Sludge	18-20	0.6 kkg	0.4 ppm	20-30%
Effluent	2-3	100 kkg	0.27 ppb	135 ppm

* Based on one kkg of product.

The results obtained indicate that on the order of 75 percent of the PCBs entering a paper mill exit associated with the product. The values selected probably represent more of a "best case" situation for a recycling plant than a typical situation within the industry. The PCBs distribution should vary from plant to plant and from product to product, but should not be nearly so widely variable as suspended solids or PCBs concentrations, which are known to fluctuate widely from day to day in a given plant.

6.0 CONCLUSIONS

The following conclusions are based on the evidence presented in this report:

- (1) The recycling of NCR carbonless copy paper was and still is the only major source of PCBs into the paper industry.
- (2) PCB levels in paper products have been decreasing since 1972 and apparently will continue to decrease under the influence of continued dilution of PCBs from recycled NCR paper.
- (3) PCB levels in effluents from paper mills utilizing reclaimed fiber have been decreasing in recent years, and will continue to decrease, due to decreased PCB levels in reclaimed fiber plus application of wastewater treatment technology.
- (4) PCB levels in sludges resulting from wastewater treatment may be as high as 10 - 20 ppm. Disposal of such material should be performed with care.
- (5) Application of carbon adsorption as an end-of-pipe method for PCBs removal from wastewater in the paper recycling industry could increase product prices as much as three to five percent.
- (6) The proportions of PCBs present in intact microballoons in paper products and in paper industry wastewaters are not known. General indications are that more PCBs in the industry are encapsulated than are "free" (released from microballoons plus other sources).
- (7) The model generated to define PCBs involvement in the paper industry represents a reasonable and consistent material balance of PCBs input and output in this industry.
- (8) According to the model, PCB levels in products and effluents are sensitive only to the parameters associated with recycle of NCR carbonless copy paper containing PCBs.

- (9) The product PCB levels obtained from exercise of the model agree well with available data; the results indicate a steep drop-off following cessation of PCBs usage by NCR and a continuing, but less steep, decrease thereafter. Current product levels are in the one ppm range (recycled fiber).
- (10) Within the limitations and assumptions of the model, on the order of 75 percent of the PCBs entering the papermaking process exit associated with the products.

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Table I. Relative ($M - 1$)⁺ Peak Heights Obtained from the Reaction of OH⁻ with Equimolar Mixtures of Aromatic Compounds^{a,b}

molecule	peak ht.	molecule	peak ht.
toluene	0.4	ethylbenzene	0.5
<i>m</i> -xylene	0.8	isopropylbenzene	0.2
mesitylene	1.0	<i>n</i> -propylbenzene	0.8
2-methylthiophene	0.4	<i>sec</i> -butylbenzene	0.5
2,5-dimethylthiophene	0.5	<i>n</i> -butylbenzene	0.9
thionaphthene	0.2	3,4-dimethylcumene	0.9

^a All values \pm 20%. ^b Normalized to *m/e* 119 from mesitylene = 1.0.

drogens for any homologous series and the length of the alkyl side chain, at least for the first few family members. For example, compare the series toluene/*m*-xylene/mesitylene, isopropyl- and *sec*-butylbenzene with *n*-propyl- and *n*-butylbenzene, the series ethyl, *n*-propyl-, *n*-butylbenzene, etc. It must be emphasized that the MS 1073 is not designed for competitive kinetic studies, so that these preliminary data can be considered only qualitative at best. However, they do indicate that the relative sensitivities for low-boiling aromatics essentially do not differ by more than a factor of two or three, and there is some evidence that the response may flatten out as the molecular weight increases, probably reflecting a collision efficiency for proton abstraction approaching unity. A comprehensive study of the rates and mechanisms of OH⁻ reactions with heavy aromatic derivatives is being undertaken at NBS using ion cyclotron resonance mass spectrometry, and hopefully these future results will provide definitive information concerning possible quantitation of fuel samples by the OH⁻ CI technique.

CONCLUSION

The use of N₂O-hexane mixtures to generate OH⁻ reagent ions provides a very useful and rapid method for screening and characterizing the aromatic compounds in fuel samples. When measurements are taken at low partial pressures of N₂O, the resulting spectra are undistorted by secondary reactions, and the patterns appear to afford the same type of information provided by low voltage electron impact with the exception that benzene and naphthalene are not detected. An advantage of the technique is the fact that the fuel samples can presumably be dissolved directly in any aliphatic solvent, without any loss of low-boiling components, and immediately analyzed without any pre-separation of the saturate fraction. Extension of the method to compound classification will require a more thorough examination of the relative rates of reaction of OH⁻ with substituted aromatics and heterocyclics.

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Interlaboratory Study of the Determination of Polychlorinated Biphenyls in a Paper Mill Effluent

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Six laboratories collaboratively studied a method for determining polychlorinated biphenyls (PCBs) in paper mill effluent. In preliminary studies, the recovery and relative standard deviation (RSD) for the PCB Aroclor 1242 added to and extracted from distilled water were 95.6% and 14.7%, respectively. Because the RSD of data from direct injection of Aroclor 1242 solutions into the gas chromatograph was of similar magnitude, 15.6%, gas chromatographic analysis appeared to provide the principal source of variation in the overall determination. Participating laboratories achieved an average 93.7% recovery of Aroclor 1242 added to a paper mill effluent; their data had a RSD of 16.0%. The results indicate that the method is satisfactory for use with paper mill effluents having PCB concentrations above 2 μ g/L and it compares favorably with findings from studies in other environmental matrices. Greater variation might be expected from effluents containing significant interferences.

Polychlorinated biphenyls (PCBs) were formerly used in carbonless copy papers, but this practice was terminated in 1971 (1, 2). Small amounts of PCBs, particularly the Aroclor 1242 mixture, are still entering paper mills which recycle used paper fibers as part of their manufacturing process. It has not been logistically nor economically feasible to completely separate carbonless copy paper from the other waste papers that are being recycled (1). Thus, until all of the PCB-containing papers still in circulation cease to appear in recycled fiber, small quantities of PCBs will continue to be discharged in the mills' aqueous effluents. The amounts of PCBs discharged can be lowered by reducing the suspended solids in the effluent from the mill (3).

A procedure for determining PCBs in industrial effluents has been issued by the Environmental Protection Agency (EPA) (4). In our collaborative investigation, we modified the EPA method to apply specifically to paper mill effluents and

aimed to document the precision of the modified method when used in several laboratories. However, the modified method described here has not been submitted to the EPA for approval—an action that would be necessary if the data were to be included in an EPA-required monitoring program. Participants in the study included industry, universities, independent laboratories, and government agencies.

The promulgated EPA method for determining PCBs in industrial effluents involves liquid-liquid extraction. Florisil cleanup (Florisil is a registered Trade Mark of the Floridin Company, Pittsburgh, Pa. 15235), and electron capture gas chromatography. Previous work has revealed deficiencies when this procedure is used on in-mill process streams containing large amounts of cellulose fibers (2). Complete removal of the PCBs from cellulose fiber suspensions required alcoholic KOH reflux of the isolated fibers subsequent to liquid-liquid extraction. Samples of paper mill effluent for PCB monitoring are typically taken following waste treatment. Because a large percentage of the suspended fibers is removed in the treatment system, these samples should not require PCB isolation procedures beyond those specified in the EPA method (4). Therefore, the procedure used in this investigation retained many features of the EPA method (4) and was judged suitable by the collaborators for the purposes of this study. As described below, some modifications were incorporated to make the method easier to use on effluents in which organochlorine pesticides were not expected or generally observed in previous analyses.

EXPERIMENTAL

The interlaboratory study was performed in two parts. Phase 1 was designed to determine the comparability of PCB methodologies in use in each laboratory and to assess the ability of the participating analysts to perform the basic operations employed in PCB determinations. Phase 2 consisted of application of the modified method to determination of Aroclor 1242 in a paper mill effluent.

Phase 1. Each participating analyst was provided with septa-sealed vials containing acetone solutions of Aroclor mixtures. Each laboratory was asked to analyze the PCB mixture by (a) direct injection into a gas chromatograph (GC) employing an electron capture detector, and (b) addition of 1 mL of the unknown to 1000 mL of distilled water followed by solvent extraction, concentration, and then injection into the GC. Procedures for these operations were left to the discretion of the analysts.

Phase 2. Validation of Sample Preparation Procedure. Prior to collection of paper mill effluent samples to be used for the PCB determinations, a separate study was performed to evaluate the study coordinator's ability to provide equivalent effluent samples to each participant. Because PCBs tend to sorb onto suspended solids, samples for collaborative study must contain equivalent suspended solids contents. A large volume of paper mill effluent was placed in a metal container and was mechanically stirred. Aliquots (250 mL) were removed and sequentially added to each of ten separate 2.5-L glass containers. (Bottles were rinsed with hexane several times to remove possible contaminants before being used for paper mill effluent samples. The hexane was drained and the bottles air dried prior to use. Aluminum foil was used to line the bottle caps.) The process was repeated ten times until each 2.5-L container was filled. Suspended solids were determined on the contents of each container.

Instructions to Analysts. Each analyst received two 2.5-L paper mill effluent samples and three sealed glass ampules containing Aroclor 1242. Two of the three ampules contained Aroclor 1242 in isooctane; one ampule was designated a "known" and contained 13.6 $\mu\text{g}/10\text{ mL}$; the second ampule was an "unknown" and contained 35.2 $\mu\text{g}/10\text{ mL}$. Participants were asked to analyze each solution by direct injection into the GC. The third ampule contained an unknown concentration of Aroclor 1242 in methanol and was to be added directly to one of the two paper mill effluent sample bottles. The ampule was designed to deliver 6.8 μg of Aroclor 1242 directly into the paper mill effluent sample bottle.

The study plan called for each participant to divide the contents

of one of the paper mill effluent samples into two equal portions. Then, each portion was to be extracted and the Aroclor 1242 concentration of each portion determined by GC. Each analyst was also instructed to add the ampule containing the 6.8 μg of Aroclor 1242 to the second 2.5-L sample container, break the ampule inside the container, mix well, and let this "spiked" sample stand for 24 h before beginning extraction and analysis by GC. As before, this "spiked" effluent sample was also to be analyzed in duplicate by dividing the 2.5-L sample into two equal portions with each one being analyzed separately.

Determination of PCBs in Paper Mill Effluent. In the promulgated method for PCBs in industrial effluents (4), PCBs and organochlorine pesticides are coextracted from the sample by liquid-liquid extraction. A silica gel microcolumn procedure and standard Florisil column cleanup are prescribed for separating PCBs from pesticides and for dividing the pesticides into subgroups. Because pesticides are unlikely constituents of paper mill effluents and were not of concern here, the EPA method (4) was modified for use in this study by removing from the procedure those steps necessary for extraction, separation, and determination of pesticides. The features of the EPA method (4) which were modified for application to paper mill effluent in this investigation are:

(1) Hexane and petroleum ether (30–60 °C) were independently shown by the collaborators to be suitable alternates to 15% methylene chloride in hexane for separatory funnel extraction of effluent. Hexane extraction has been shown to recover PCBs almost quantitatively from effluents with low fiber contents (2). Solvents of higher polarity, such as methylene chloride in hexane, extract excessive amounts of non-PCB materials without improving PCB recovery.

(2) To assure consistent performance of the electron capture detector and to minimize down time for detector cleaning, all extracts were subjected to Florisil column cleanup prior to gas chromatographic analysis.

(3) In addition to the specifications for Florisil columns (4), other column sizes and amounts of Florisil and eluting solvent were acceptable for PCB determination provided that (a) all PCBs were completely eluted, and (b) chromatogram quality signified that samples had been adequately cleaned up. Elution of PCBs from the Florisil column with hexane or petroleum ether as well as with 6% ethyl ether in petroleum ether was permitted. Use of petroleum ether alone for elution is standard practice in determining PCBs in paper and paperboard (5).

(4) The silica gel microcolumn procedure for separating PCBs from pesticides was deleted from the method.

(5) Gas chromatographic column liquid phases specified in the EPA method (4) include SE-30 or OV-1, and OV-17/QF-1. Other silicone liquid phases used successfully for determining PCBs in Phase 1 of this study included OV-17, OV-210, DC-200, OV-101, OV-225, and equivalent SP phases. An earlier collaborative study has indicated that several column materials are useful for PCB determinations (6). Therefore, the phases listed above were considered acceptable for this study. Also accepted were stainless steel as well as glass columns.

(6) Unknown Aroclors were identified by matching retention times and relative peak heights with peaks in reference Aroclors. To ensure valid quantitation, amounts were injected such that the size of the peaks from the sample and the standard were within $\pm 25\%$. When quantitation was based upon peak heights, at least four peaks were used.

RESULTS AND DISCUSSION

Phase 1. The results of the GC analyses of Aroclor 1242 in acetone are presented in Table I. The average PCB concentration (as Aroclor 1242) based on direct injection into the GC was 1.47 $\text{ng}/\mu\text{L}$, representing an average recovery of 98% of the 1.5 $\text{ng}/\mu\text{L}$ present in the acetone solution. Therefore, on the average, the results indicated that the eight participants in Phase 1 had good GC technique and could quantify PCBs.

While the results of the direct injection experiment were good, some variation among the analysts was evident as shown by the standard deviation (0.23 $\text{ng}/\mu\text{L}$), relative standard deviation (RSD) (15.6%) and range (1.05–1.76 $\text{ng}/\mu\text{L}$). While

Table I. Determination of PCBs as Aroclor 1242 in Acetone Solution by Direct Injection and Extraction from Distilled Water (Phase 1)

analyst	PCB by direct injection, ng/ μ L ^a	PCB extraction from distilled water, %
1	1.52	90.0
2	1.41	99.3
3	1.46	89.6
4	1.70	>100 ^c
5	1.59	114
6	1.26	106
7	1.76	70.1
8	1.05	100
average	1.47 ng/ μ L ^b	95.6% ^d
range	1.05-1.76 ng/ μ L	70.1-114%
standard deviation	0.23 ng/ μ L	14.1%
rel. std. deviation	15.6%	14.7%

^a Concentration of Aroclor 1242 = 1.50 ng/ μ L.^b Represents average finding by direction injection = 98%.^c Treated as outlier as analyst was unable to quantitate recovery except as reported. ^d Data from analyst no. 4 excluded in statistical calculations.**Table II.** Test for Determining Suspended Solids Concentrations in Representative Samples

run	suspended solids, mg/L
1	73.2
2	80.8
3	74.8
4	74.8
5	75.3
6	73.6
7	77.6
8	77.6
9	74.4
10	72.4
average	75.5 mg/L
range	72.4-80.8 mg/L
std. deviation	2.53 mg/L
rel. std. dev.	3.3%

this indicated more variation than might be desired in an interlaboratory study, it is shown later that a RSD of 15.6% is typical for PCB determinations involving environmental matrices.

The extraction of Aroclor 1242 added to distilled water resulted in an average recovery of 95.6%. This was satisfactory, although the variation was again relatively high as

indicated by the RSD (14.7%) and the range (70-114%). Because this sample was free from interferences, the precision represents that which is attainable under unusually favorable analytical conditions.

The RSDs obtained in the direct injection experiment and in determination of Aroclor 1242 added to distilled water were of similar magnitude. This suggests that GC analysis provided the major sources of between-laboratory variation in the overall analytical scheme. Likely contributors to this variation included: (a) use of different Aroclor 1242 standards with slightly different PCB isomeride composition, and (b) use of different quantitation methods, including measurement of peak heights, peak areas, or weight percentages of individual peaks (7-9). The contribution of different GC columns and conditions is difficult to assess, although it was possibly advantageous for the analysts to use their own columns which produced familiar Aroclor chromatograms.

Phase 2. This phase of the study again involved determination of Aroclor 1242 by direct injection of solvent solutions into the GC and, of greater importance, also included determination of Aroclor 1242 in a paper mill effluent. The effluent was studied as collected and after addition of a known amount of an Aroclor 1242 standard.

The ability of the proposed sample collection procedure to supply equivalent mill effluent samples for collaborators was tested by determining if the procedure could provide samples of equivalent suspended solids content. Results are given in Table II. One analyst removed aliquots from each of ten different 2.5-L sample bottles, filled as described earlier, and performed the standard suspended solids measurement (10). The data indicate that representative suspended solids distribution could be achieved by the sampling technique, since the RSD experienced was 3.3%. The published RSD for suspended solids determinations ranges from 0.16 to 35% depending on the actual suspended solids concentration present in the sample (10).

Known and unknown Aroclor 1242 concentrations were determined by direct GC injection from glass ampules. The results are shown in Table III. The known solution allowed participating analysts to check their in-house standards with one prepared by the coordinating laboratory and also provided a reference standard to be used for the spiking, extraction, and recovery experiment involving the paper mill effluent sample.

The determination of the known and unknown PCB concentrations by direct injection into the GC yielded essentially the same average calculated recovery data, i.e., 98% and 97%, respectively (Table III). However, the variation among seven reporting analysts was somewhat greater for the unknown standard solution (RSD = 12.6%) than for the known standard solution (RSD = 7.5%). There is no im-

Table III. Determination of PCBs as Aroclor 1242 in Isooctane Solution by Direct Injection (Phase 2)

analyst	PCB concentration as Aroclor 1242			
	known (13.6 μ g/10 mL)		unknown (35.2 μ g/10 mL)	
	concn reported, μ g/10 mL	calcd recovery, %	concn reported, μ g/10 mL	calcd recovery, %
1	14.2	104	37.0	105
2	13.6	100	34.0	97
3	12.5	92	36.0	102
5	12.5	92	27.3	78
6	12.8	94	31.0	88
7	15.0	110	40.7	116
8	12.5	92	33.4	95
average	13.3 μ g/10 mL	98%	34.2 μ g/10 mL	97%
range	12.5-15 μ g/10 mL	92-110%	27.3-40.7 μ g/10 mL	78-116%
std. dev.	1.0 μ g/10 mL	7.2%	4.3 μ g/10 mL	12.2%
rel. std. dev.		7.5%		12.6%

Table IV. Determination of PCBs as Aroclor 1242 in a Paper Mill Effluent (Phase 2)

analyst	replicate, $\mu\text{g/L}$		average PCB concn reported by each analyst, $\mu\text{g/L}$
	no. 1	no. 2	
1	2.70	2.09	2.40
2	3.48	3.88	3.36
3	2.45	2.89	2.67
6	2.26	2.32	2.36 ^a
7	2.33	2.73	2.53 ^a
8	2.98	2.84	2.95 ^a
average ($n = 12$)		2.74 $\mu\text{g/L}$	2.71 $\mu\text{g/L}$ ^b
range		2.09–3.88 $\mu\text{g/L}$	2.36–3.36 $\mu\text{g/L}$
std. dev.		0.52 $\mu\text{g/L}$	0.39 $\mu\text{g/L}$
rel. std. dev.		19.0%	14.4%

^a Includes small additional amount of PCB obtained by rinsing sample bottle with solvent after removal of sample.

^b Statistics developed by considering only the average PCB concentration reported by each analyst.

mediate explanation for this except that the unknown solution was ca. 2.5 times more concentrated than the known solution. This resulted in an additional dilution step to keep the unknown Aroclor on scale. This could have introduced additional error and the slightly higher RSD.

The PCB concentration in the paper mill effluent was determined in duplicate by six analysts according to the modified analytical procedure. The results are given in Table IV. The paper mill effluent was also analyzed in duplicate following addition of a methanol-based Aroclor 1242 standard. These data appear in Table V. Relative standard deviations of the PCB determinations performed on the effluent as collected and following addition of Aroclor 1242 were 19.0% and 16.0%, respectively.

The variations in the results for the determination of Aroclor 1242 in the paper mill effluent among the six analysts who completed Phase 2 were not very different from the variations noted for the direct GC injection of Aroclor 1242 solutions (Tables I and III). This suggests, as did the Phase 1 findings, that only small additional errors were introduced by the sample extraction and Florisil cleanup steps.

As indicated in Table V, the average recovery of the added Aroclor 1242 was 93.7%. This average is slightly misleading since three results clustered near 100% and the remainder ranged from 84 to 88%.

Following Florisil cleanup of the paper mill effluent used in this study, all collaborators obtained characteristic Aroclor 1242 chromatograms. Some other paper mill effluents contain interfering materials that cannot be removed on Florisil and

Table VI. Some Examples of Interlaboratory Variation Based on Collaborative Studies Involving PCBs

sample matrix	rel. std. dev., %	no. of analysts	ref.
paperboard	15–22	11	(6)
milk	18–31 ^a	10	(9)
chicken fat	6–16 ^a	10	(9)
marine wildlife	21	14	(12)
shark liver homogenate	27	6	(13)
marine sediments	22	10	(14)
fish	27–37	7–13	(15)
paper mill effluent	15–19	6	this study

^a RSD varied with method used for GC quantitation.

which produce badly distorted chromatograms (11). Between-laboratory variation in PCB determinations conducted on effluents containing intractable interferences would undoubtedly be greater than that experienced in the current investigation.

Other observations reported by the collaborators in Phase 2 included (a) formation of emulsions during solvent extraction of the effluent, and (b) small differences in peak ratios between the individual laboratory's Aroclor 1242 standards and the standard provided by the coordinating laboratory. Emulsions were broken by centrifugation or addition of Na_2SO_4 . The problem of variations in PCB standards could be obviated by providing Aroclor standards from a common source to all laboratories conducting PCB determinations.

Considering the nature of the paper mill effluent matrix, the results of this interlaboratory study were good. This can be substantiated by comparison of the RSDs reported in this study with those reported for PCB collaborative studies involving other complex environmental matrices (Table VI). It is clear, however, that analysts desiring to compare their results for the determination of PCBs in environmental samples must anticipate variations within the range of 15–20% expressed as the RSD.

CONCLUSIONS

Based on this interlaboratory study, the method described herein for PCBs in paper mill effluents appeared satisfactory. However, the statistics developed in this work were derived from determination of Aroclor 1242 mixtures in the concentration range of 2–6 $\mu\text{g/L}$ and on an effluent from which interferences were readily removed. Different precision and accuracy findings could occur when the method is applied to paper mill effluents having different contents of PCBs and of materials which interfere in the determination. Gas chromatographic standards and techniques appear to have been the principal sources of variation in this study. It is

Table V. Determination of PCBs as Aroclor 1242 in a Paper Mill Effluent to Which a Standard Solution of Aroclor 1242 Was Added

analyst	replicate, $\mu\text{g/L}$		average PCB concn reported by each analyst, $\mu\text{g/L}$	calcd recovery of std. PCB, %
	no. 1	no. 2		
1	4.30	4.90	4.60	88
2	6.26	5.95	6.10	100
3	6.56	4.50	5.53	103
6	4.32	4.15	4.32 ^a	84 ^a
7	5.80	4.96	5.42 ^a	101 ^a
8	4.64	5.17	4.96 ^a	86 ^a
average ($n = 12$)		5.13 $\mu\text{g/L}$	5.16 $\mu\text{g/L}$ ^a	93.7% ^c
range		4.15–6.56 $\mu\text{g/L}$	4.32–6.10 $\mu\text{g/L}$	84–103%
std. dev.		0.82 $\mu\text{g/L}$	0.63 $\mu\text{g/L}$	8.53%
rel. std. dev.		16.0%	12.2%	9.1%

^a Includes small additional amount of PCB obtained by rinsing sample bottle with solvent after removal of sample.

^b Based on average PCB concentration reported by analysts in Table IV. ^c Statistics developed by considering only the average PCB concentration reported by each analyst.

important that regulatory officials seeking to establish effluent standards for PCBs in discharge media such as paper mill effluent take the findings of this and other related studies into consideration, so that the standards may be enforced rationally in light of analytical variability.

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Quaternized Porous Beads for Exclusion Chromatography of Water-Soluble Polymers

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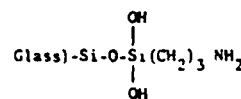
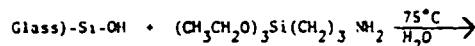
The novel approach of using ion-exchange chromatographic supports for size exclusion chromatography of neutral and cationic water-soluble polymers is presented. A quaternary ammonium group, a strong anion exchanger, has been bonded to the surface of porous silica glass in the pore size range from 40 to 25 000 Å. Chromatograms are shown of poly(2-vinylpyridine) and dextran molecules using acidic salt solutions as eluents. Molecular weight calibration graphs, theoretical plate height plots, and concentration effects are discussed in detail.

Gel permeation chromatography (GPC), originated in 1965 by J. Moore (1), has primarily focused on nonaqueous applications and many advances have been achieved. However, progress in the area of aqueous exclusion has not been as rapid owing to the many experimental difficulties encountered (2). Aqueous GPC has been confined to neutral and anionic polymers since commercially available supports work favorably for a number of these materials (3). Cationic polymers have not been chromatographed because porous silica glasses and cross-linked copolymer resins tend to be anionic in nature leading to solute support interactions. G. B. Butler (4), in 1976, chromatographed cationic polyelectrolytes on quaternized styrene/divinylbenzene supports with limited success. Some of the disadvantages observed were: (1) the swelling of the resin which was a function of ionic strength; (2) the support compression as the flow rate increased; (3) the limited porosity of these supports. The porous silica glass supports were felt to serve as the ideal substrate if adsorption could be eliminated. They have a fixed pore and particle size and can be used at the high flow rates needed for microparticulate high resolution chromatography. Attempts to deactivate the surface by silanization (5) and by the addition of cationic surfactants to the eluent (5, 6) have been unsuccessful. In this paper, we are introducing the concept of using ion-exchange supports on glass to reduce solute-glass interactions (7).

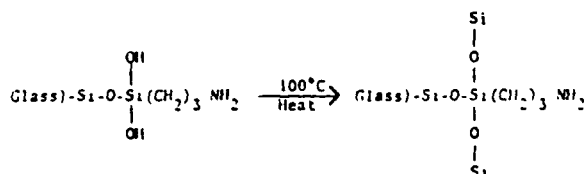
The ion-exchange support chosen to chromatograph cationic polymers must be a strong anion exchanger. The quaternary

ammonium ion is an excellent choice since it creates a positively-charged surface to repel the positively-charged polyelectrolyte. The support was prepared by reacting 3-aminopropyltriethoxysilane with the glass followed by reaction of the terminal NH_2 group with 3-chloro-2-hydroxytrimethylammonium chloride. The procedure was similar to those described in the literature for the silanization of glasses (2, 8, 9) and is illustrated in the equations below:

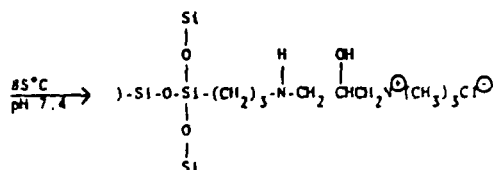
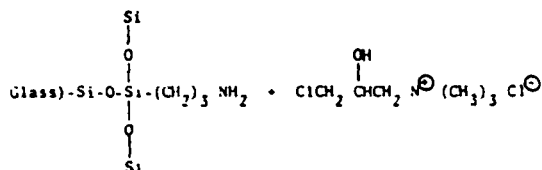
(1)



(2)



(3)



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Determination of polychlorinated biphenyls in paper mill effluents

The Influence of suspended solids

ABSTRACT

Complete extraction of Aroclor 1242 (a mixture of polychlorinated biphenyls) from paper mill effluents and process streams containing cellulose fibers required a two-step procedure. The steps were (1) triple separatory funnel extraction and (2) subsequent alcoholic KOH reflux of the isolated fibers. Much of the PCB in a fiber-water suspension was sorbed onto the fibers. Alcoholic KOH reflux was needed because a portion of the sorbed PCB was resistant or inaccessible to the solvent in the separatory funnel extraction. Contributing to PCB sorption and retention were fiber-specific surface area and resin content. Separatory funnel extraction effectively recovered Aroclor 1242 from suspensions containing pigments.

KEYWORDS

Polychlorinated biphenyls
Chemical analysis
Cellulose fibers
Effluents
Reclaimed fibers
Paper mills
Gas chromatography
Surfactants

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Polychlorinated biphenyls (PCB's) are organic compounds which have been sold in the United States as mixtures, called Aroclors. Prior to the spring of 1971, carbonless copy paper contained Aroclor 1242. However, this use was terminated when PCB's were found to possess low-level toxicity. Old carbonless copy paper containing Aroclor 1242 is apparently still entering paper mills using recycled fiber with their raw ma-

terials, and the PCB's leave the mills in their products, effluents, and sludges.

Regulations designed to minimize the entry of PCB's into the environment via aqueous effluents have been, or soon will be, promulgated by both federal and state agencies. Consequently, accurate methods for PCB determinations are needed for effluent monitoring and for in-plant use in evaluation of control technology. The method pro-

scribed by the Environmental Protection Agency (EPA) for determining PCB's in industrial effluents (1) involves liquid-liquid extraction, Florisil cleanup, and electron capture gas chromatography. In the current investigation, the effectiveness of this methodology in analysis of paper mill effluents and process streams containing suspended solids has been evaluated. Of principal interest has been the retention of PCB's by suspended cellulose fibers during separatory funnel extraction.

1. Recovery of Aroclor 1242 from spiked woodpulp and from submitted fiber suspensions

Sample	Consistency, %	Recovery by separatory funnel extraction, %	Recovery by alcoholic KOH reflux, %
Hardwood A	1.0	84.6	11.6
Hardwood B	0.7	91.0	0.8
Hardwood C	0.7	82.2	11.2
Softwood A	0.8	101.0	—0
Softwood B	0.7	83.0	5.8
Softwood C	0.7	84.2	1.2
Mill sample	0.4	91.5	8.5
Mill sample	0.06	94.4	5.6
Mill sample	—	85.0	15.0

Isolation of PCB's from samples containing cellulose fibers

Known amounts of Aroclor 1242, 100 µg/liter, were added to 0.7–1.0% suspensions of several hardwood and softwood pulps in water. Incomplete recoveries were usually experienced when these suspensions were subjected to triple separatory funnel extractions with hexane, as indicated by the data in Table I. Improvements in recovery did not occur



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II. Recovery of Aroclor 1242 from hardwood fiber suspensions

Fiber content, %	Recovery by extraction, %	Recovery from fibers, %	Total recovery, %
0.005	97.0	0.9	97.9
0.01	96.4	2.4	98.8
0.05	91.8	8.4	100.2
0.10	91.8	10.6	102.6
0.16	84.2	9.0	93.2
0.40	80.2	15.8	96.0
0.60	80.0	15.5	95.5
0.80	80.4	15.6	96.0

III. Recovery of Aroclor 1242 from softwood fiber suspensions

Fiber content, %	Recovery by extraction, %	Recovery from fibers, %	Total recovery, %
0.005	95.9	0.5	96.4
0.01	94.2	0.5	94.7
0.05	93.8	1.1	94.9
0.10	98.6	1.5	100.3
0.10	85.4	2.6	88.0
0.40	84.4	2.8	87.0
0.80	81.4	5.6	87.0
0.80	82.2	5.9	88.1

when 15% methylene chloride in hexane was used as extracting solvent. Use of more polar solvents, such as ethyl ether-petroleum ether mixtures, was impractical; they removed excessive amounts of non-PCB materials which interfered with subsequent gas chromatographic analysis. Following the separatory funnel extraction, the fibers were filtered from the samples, and the residual PCB was removed from the fibers by reflux in 2% alcoholic KOH, as is normally used for determining PCB's in paperboard (7). Amounts of PCB recovered in this manner are also shown in Table I. Removal of all residual PCB by the alcoholic KOH was demonstrated by dissolving the fibers in 72% H₂SO₄, diluting with water, and extracting with hexane.

Included also in Table I are extraction data obtained on typical fiber suspensions submitted by a paper mill for PCB determination. Results in that table indicate that complete removal of Aroclor 1242 from suspensions of cellulose fibers required a two-step procedure. The steps are (1) triple separatory funnel extraction, and (2) subsequent alcoholic KOH reflux of the isolated fibers.

Data in Tables II and III resulted from a study designed to determine whether alcoholic KOH reflux of the fibers subsequent to separatory funnel extraction was needed to remove PCB's from fiber-water suspensions with low fiber contents. The results indicate that fibers, even at low concentrations in the sample, retained some PCB's, and that alcoholic KOH reflux was needed for complete PCB removal. However, in analysis of effluents containing less than about 0.06% hardwood or 0.5% softwood fibers, the amount of PCB retained by the fibers was small compared with other reported sources of error in PCB determinations [e.g., 20% relative standard deviation for chroma-togram quantitation (3)].

Thus, it may be concluded that the liquid-liquid extraction technique should be adequate for most effluents containing low amounts of suspended solids, and that it is inadequate for process streams containing large

amounts of cellulose fibers. Because of their higher fiber contents, the process streams would require the two-step procedure for complete PCB removal.

Effects of fiber properties on PCB distribution

The hardwood pulp in Table II apparently retained more Aroclor 1242 during separatory funnel extraction than did the softwood pulp in Table III. Perhaps that result was influenced by the higher hydrodynamic specific surface area of the hardwood (19,880 vs. 15,100 cm²/g). Those findings prompted consideration of the impact of fiber properties on distribution of PCB's between fibers and water.

For initial studies of PCB distribution, a bleached softwood pulp was beaten and classified. Using the constant-rate filtration technique, the hydrodynamic specific surface of the on-10 mesh fibers and the through-65 mesh fines were found to be 9,580 and 120,000 cm²/g, respectively. Identical alcohol-benzene extractives, 0.2%, were measured on each of the two fractions. Suspensions, 0.78% consistency for the long fibers and 0.426% for the fines, were spiked with 100 µg/liter of Aroclor 1242 and stirred for 3 min. As discussed subsequently, testing of these samples was performed in two different ways: One series of samples was filtered before separatory funnel extraction of PCB's, and the second series of samples was filtered after separatory funnel extraction.

Samples in the first series were filtered, and the PCB was removed from the filtrate by separatory funnel extraction with petroleum ether and from the fibers by alcoholic KOH reflux. Data on these samples in Table IV indicate that the fines sorbed more PCB than did the long fibers. If the fines consistency had been as high as that of the fibers, that trend would quite likely have been even more emphatic. The PCB sorbed by the long fibers and fines was computed to be 1,680 and 13,700 ng/g o.d. fiber, respectively. Thus, the ratio of the amounts of PCB sorbed by the two fractions was roughly propor-

IV. Distribution of Aroclor 1242 on fibers and fines before and after separatory funnel extraction

	On-10 mesh	Through-65 mesh
Filtration before extraction		
Recovery from filtrate, %	78.2	12.3
Recovery from fibers, %	21.8	87.7
Filtration after extraction		
Recovery by extraction, %	100	81.8
Recovery from fibers, %	0	18.2

tional to the ratio of their hydrodynamic specific surfaces (about 1:10). Subsequent to this investigation, sorption of Aroclor 1242 by cellulose fibers was found to continue for several hours (4). If these suspensions had been stirred longer before filtration, amounts of PCB on the fibers and fines would probably have been greater.

Samples in the second series were filtered after separatory funnel extraction with petroleum ether, yielding results also shown in Table IV. Methodology for these analyses was, therefore, identical with that used to obtain data in Tables I-III. These data show that the separatory funnel extraction removed all of the sorbed PCB from the long fibers and most, but not all, of the PCB from the fines. The PCB not extracted from the fines was in some manner resistant or inaccessible to the extracting solvent. It might be speculated that a portion of the porous structure of the fines was not penetrated by droplets of petroleum ether during separatory funnel extraction of the aqueous slurry. It is because of this resistant or inaccessible PCB that the two-step extraction procedure must be used in order to remove all of the PCB from suspensions containing cellulose fibers and fines.

Additional insight into ease of ex-

V. Distribution of Aroclor 1242 between water and fibers, filtered before analysis

	Recovery from filtrate, %	Recovery from fibers, %
As received		
Bleached softwood	92.0	37.5
Bleached hardwood	37.0	57.5
Unbleached softwood	24.0	62.6
Unbleached hardwood	31.0	52.0
Pre-extracted		
Bleached softwood	70.4	16.8
Bleached hardwood	71.4	12.6
Unbleached softwood	23.0	59.6
Unbleached hardwood	56.0	29.0

VI. Recovery of Aroclor 1242 using two-step extraction procedure

	Recovery by extraction, %	Recovery from fibers, %
As received		
Bleached softwood	90.9	9.1
Bleached hardwood	40.4	13.4
Unbleached softwood	92.7	4.6
Unbleached hardwood	87.3	11.0
Pre-extracted		
Bleached softwood	98.8	2.4
Bleached hardwood	96.0	2.2
Unbleached softwood	94.4	4.4
Unbleached hardwood	98.6	4.6

VII. Effect of surfactant in extraction of Aroclor 1242 from fiber suspensions

	Recovery by separatory funnel extraction, %	Recovery by alcoholic KOH reflux, %
Softwood D	117.0	5.8
Softwood D + surfactant	98.4	3.4
Softwood C	14.2	1.2
Softwood C + surfactant	67.8	3.0
Hardwood C	82.2	11.2
Hardwood C + surfactant	88.6	7.0

traction of PCB's from wood pulps was obtained from studies involving unbleached and bleached hardwood and softwood pulps made in the same mill. Alcohol-benzene extractive contents of the unbleached pulps were both 0.38%; they were 0.46% and 0.23% for the bleached hardwood and softwood, respectively. The pulps had generally similar hydrodynamic specific surface areas, ranging from 10,000 to 13,800 cm²/g. Aqueous suspensions of 0.1% consistency were prepared from each of the pulps as received and following removal of alcohol-benzene extractives. Aroclor 1242 amounting to 10 µg/liter was dispersed in each sample, and the suspensions were allowed to stand for one-half hour. PCB's were then isolated from the samples using the two procedures employed previously: (1) filtration before extraction, with the filtrate extracted in a separatory funnel, and the fibers refluxed in alcoholic KOH, and (2) filtration after the suspension had been extracted in the separatory funnel, with subsequent reflux of the fibers in alcoholic KOH (the two-step extraction procedure).

Data are shown in Tables V and VI. These data confirm earlier results indicating that separatory funnel extraction of fiber suspensions removed most but not all of the PCB sorbed onto the fibers. With the exception of the unbleached softwood pulp, removal of alcohol-benzene extractives reduced the apparent tendency of Aroclor 1242 to sorb onto fibers (Table V) and to be retained by fibers during separatory funnel extraction of the suspension (Table VI). Thus, resin content of the pulp usually affected PCB sorption and retention. Because PCB's have low polarity, their sorption was probably facilitated by the low-polarity resins.

In Table VI it is shown that significant amounts of Aroclor 1242 were retained on the fibers during separatory funnel extraction even after resinous materials were removed from the pulps by pre-extraction. This suggests that pulp structure or chemical makeup, in addition to resin content, affected PCB inaccessibility or resistance to extraction. The greater amounts of PCB retained by the unbleached, pre-extracted pulps suggest a possible effect of lignin.

With the unbleached softwood pulp, features other than resin content appeared to be predominant in PCB distribution and retention; pre-extraction of this pulp had little effect in either Table V or VI.

Effect of surfactants

A survey of several surfactants revealed that the nonionic surfactant Triton X-100 (Rohm & Haas Co.) shifted the distribution of Aroclor 1242 so that more PCB was in the aqueous phase and less on the cellulose fibers. Therefore, it was hoped that addition of this surfactant to fiber suspensions would permit all of the PCB to be removed during separatory funnel extraction and would obviate the second step of the two-step extraction.

Suspensions of three bleached pulps at 0.7% consistency were spiked with 80 µg/liter of Aroclor 1242 and were extracted using the two-step procedure. Samples of each pulp were prepared with and without 0.02% Triton X-100, based on the total suspension. Data in Table VII indicate that surfactant addition reduced the amount of PCB retained by the fibers. However, the alcoholic KOH reflux of the fibers was still needed for complete PCB removal.

Other suspended solids

The effectiveness of separatory funnel extraction for removal of PCB's from noncellulosic suspended solids in paper mill effluents and process streams was also evaluated. No cellulose fibers were present in these laboratory samples. However, the starch and pigments to be studied were added in amounts comparable to what might be found in a papermaking furnish.

Recoveries of 10 µg/liter of Aroclor 1242 spikes from each step of the two-step extraction procedure are shown in Table VIII. Nearly all of the PCB was recovered by separatory funnel extraction, and no detectable PCB was isolated by alcoholic KOH reflux of the filtered starch and pigments. Thus, apparently no significant amount of the PCB in suspensions of these noncellulosic solids was resistant or inaccessible to solvent extraction in the separatory

VIII. Extraction of Aroclor 1242 from suspensions of noncellulosic materials

Sample	Concentration µg	Recovery by separatory funnel extraction, %	Recovery by alcoholic KOH reflux, %
Starch	0.15	94.6	~0
Kaolin clay	1.25	93.8	Interference
TiO ₂	0.25	96.4	~0
Talc	1.25	94.2	Interference



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funnel. Unfortunately, gas chromatograms showed non-PCB interferences from the clay and the talc which might have obscured detection of small amounts of Aroclor 1242. Recoveries of less than 100% by separatory funnel extraction probably reflect manipulative and volatilization losses, which were discussed in an earlier preliminary communication (5). The apparent low retention of PCB's by the pigments is consistent with the comparatively low affinity of PCB's for kaolin clay and other inorganics (6). The data from this investigation indicate that the cellulose fibers, rather than the noncellulosic materials, are the components of paper mill effluents and process streams which require the two-step extraction.

Recommended analytical procedures

Procedures recommended for isolating PCB's from paper mill effluents and process streams containing suspended solids consist essentially of the EPA-prescribed liquid-liquid extraction technique (1) followed by alcoholic KOH reflux of the suspended solids. The alcoholic KOH treatment has been recommended by the Food and Drug Administration for determining PCB's in paperboard (2). In this report these combined methods have been termed the "two-step extraction procedure." Omission of the second step of the procedure may be considered, depending upon the amount and type of suspended solids in the sample and the degree of accuracy required in the analysis. It is recommended that the analyst evaluate the need for the second extraction step on the types of samples which he routinely analyzes. Also recommended are the steps to minimize volatilization losses of Aroclor 1242 described in a previous communication (5).

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EPA 560/6-77-005

PCBs INVOLVEMENT IN THE PULP AND PAPER INDUSTRY

Task 4

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EPA Contract No. 68-01-3259

EPA Project Officer: Thomas Kopp

For

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ABSTRACT

The sources, distribution, and losses of PCBs in the U.S. pulp and paper industry are discussed in detail. The major source of PCBs to the industry is recycled carbonless copy paper manufactured from 1957 to 1971, but the amounts of PCBs from this source diminished rapidly after 1971. A model showing past and projected PCBs content in product and wastewaters from the industry is presented and discussed. Estimated costs (worst-case basis) for wastewater treatment to achieve one ppb PCBs in effluents from the industry are developed; results indicate a 3 to 5 percent product cost increase will result from such treatment.

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APPENDIX I

INDUSTRY INTERVIEWS AND PLANT TRIPS

I-1.0 OBJECTIVES OF INDUSTRY INTERVIEWS AND DISCUSSIONS

From previous efforts under Task I of Contract 68-01-3259, it was apparent that the data available concerning PCBs in the paper industry were sparse at best, and that extensive efforts would be required to gather sufficient information for the model development and interpretation. The gathering of such information was the major objective of all industry contacts during this work; early in the program industry was made aware of the purpose of and our approach to the work. Subsequent response and cooperation by the industry were uniformly excellent.

Specific areas covered during the interviews and discussions included:

- 1) The level of awareness of the PCB problem within the industry;
- 2) Analytical data (on PCB levels in products and effluents) which might be available or which might be obtained and made available at a later date;
- 3) The possibilities and practicalities which bear on treatment of mill effluents, or on internal water reuse and purification systems;
- 4) Present trends in treatment technology as the mills prepare for adherence to the 1977 and 1983 effluent quality criteria;
- 5) The standard practices of sampling and analysis which generate the data base of PCB levels in the plants;
- 6) The similarities and differences found between production mills operating under current bounds of raw material, energy, labor and treatment costs; and
- 7) PCBs transport within the plants.

I-2.0 MEETINGS WITH TRADE ASSOCIATIONS

I-2.1 Meeting with API

In mid-July, 1976, a meeting was held in Washington, D. C. with representatives of the American Paper Institute (API), the Boxboard Research and Development Association (BRDA), the National Council of the Paper Industry for Air and Stream Improvement (NCASI), senior staff members from several API member companies, and the EPA Office of Solid Waste Management Programs (OSWMP). The approach to the program, and particularly the PCBs-industry model, was outlined and discussed in detail. Cooperation and needed information were solicited, and plans for the provision of available or anticipated data were made. All areas noted under Section I-1.0 were covered.

I-2.2 Meeting with Institute of Paper Chemistry (IPC)

On August 6, 1976 a meeting was held with staff members of the IPC in Appleton, Wisconsin. John C. Wollwage, Vice President-Research; Dr. H. S. Dugal, Director, Industrial and Environmental Systems Division; Dwight B. Easty, Group Leader, Analytical Chemistry, Division of Natural Materials and Systems; Mr. George Dubey; and Mr. Peter Parker (all of IPC) took part in the discussions.

At that time the IPC was performing an in-house study aimed at development of an improved procedure for PCB analysis in pulp and paper mill matrices. They had attacked the question of PCB partitioning in mill flows and found PCBs to be substantive to fiber, associating most notably with the small particulate constituents (fines) of the pulp/water system. White water high in fines content is routinely recycled in order that as much of the fiber as possible eventually become products since fines have a desirable effect on the qualities of opacity and surface smoothness. Economical use of the raw fiber requires a minimization of the fines loss. Such a procedure appears to preferentially associate the major portion of any PCBs with the paper product.

It was also agreed that the PCB concentration in the waste sludge might reasonably be assumed to be at the same concentration as in the product.

In other words, if the PCB levels in paper product is in the low parts per million range, PCB levels in the sludge will also be in this range. The limited sludge data obtained supports this contention, and at the same time shows paper mill sludges to be comparable to municipal treatment plant sludges in PCB content (ranging up to 23 ppm)⁽¹⁴⁾.

The majority of PCBs introduced to papermaking as part of the wastepaper input were believed by the IPC personnel to be still enclosed in the gelatin-gum arabic microballoons. The microballoons (10 - 20 microns in diameter) are known to be substantive to fiber. They release their PCB load for analysis upon treatment with alcoholic KOH solution. It was not known what fraction of the incoming capsules may break open, nor whether the pulping and refining steps may cause breakage, but it was suspected that relatively few of the microballoons would rupture during the papermaking process.

In addition, it was decided that PCBs in intact capsules would not participate in evaporation as "free" or "wild" PCBs may be able to do. Mass balances done by IPC on some paper mills have given an indication of a possibility of evaporative losses, but not in large amounts, nor in amounts which would jeopardize the overall conclusions or credibility of the model presented in Section 5.0 of this report.

During the analytical methodology work by IPC, small amounts of PCB used to spike solutions showed significant evaporative losses. This has resulted in a strong recommendation for the minimization of sample transfers and handling in analysis for PCBs.

Present analytical capabilities at IPC show detection limits for paper to be 0.1 ppm PCB and for solutions to be 0.1 ppb PCB. Both call for a trained operator conversant with and practiced in routine PCB analysis.

Interferences on the chromatogram appear to be removed in good part by oxidation of the sample with chromium trioxide. These interferences seemed to be peculiar to the types of matrices found in pulp and paper processes. Attempts to simplify PCB analysis by perchlorination of all PCBs to decachlorobiphenyl were found to give unsuitable results. This treatment

appeared to have converted some non-PCB components of carbonless copy paper into a form which could be incorrectly identified as PCBs.

Other aspects of the problem and of the IPC program were discussed in detail. Many of these are discussed or referenced elsewhere in this report. The results of this meeting served to solidify the approach to the model and the selection of parametric values to be used in exercising the model.

I-3.0 PLANT VISITS

Seven paper mills were visited during the program; four of these utilized between 50 and 100 percent recycled material. The others either were companies known to be very much aware of the PCBs problem and using some recycled fiber or mills using only virgin fiber. Short summaries of the trip reports for these plants are included below. As will be noted, some plants are not named in these summaries.

I-3.1 Plant A - 100 Percent Recycled Raw Material

General Description

Plant A employs approximately 300 people and has a Fourdrinier, two cylinder machines and a Printer Tinter. The raw material used is wastepaper which has been sorted, graded, baled and marked by organized paper stock dealers throughout the Midwest. The most important grades used are reclaimed corrugated containers, mixed paper, newspaper and clippings trimmed from box shops and converting plants. Much of the stock is picked up in large cities by company trucks as return loads after delivery of the finished board. This re-use of secondary fibre eliminates a large amount of paper tonnage being sent to landfill or incinerated. In 1971 85,000 tons of wastepaper were reclaimed through this plant.

The basic product manufactured from the wastepaper is paperboard. This product is used for core stock, tube stock, wrapper, carton, paper box, book bindings, and globe stock.

Pulping, Cleaning and Refining

The first step in converting paper stock to pulp is called hydration; machines called hydropulpers are used. These are large tubs with a rotating disc in which the dry paper is mixed with warm or hot water. Chemicals may be added to aid in the dissolving process and to destroy any bacteria which may be present. Most of these machines operate on a continuous process. As soon as the fibers are dissolved fine enough to be extracted through 1/8" holes they are screened off.

The various cleaning and refining processes which follow pulping are typically a spin-off to remove light particles of foreign material, and settling to remove heavy dirt. In addition, there are several systems of mechanical screening to remove coarse or undefibered bundles and dirt. Not the least important is a treatment of high pressure - high temperature steam followed by a refining process for the purpose of breaking down foreign materials like pitch, wax, or asphalt which may be found in the wastepaper.

After the paper stock is cleaned and defibered, it is stored as a liquid suspension in large chests. Before going to the paper machine the stock is again refined or "brushed out" in machines called Jordans or Refiners, mixed to an exacting consistency with water and screened one last time.

Papermaking

Plant A employs both Fourdriner and cylinder-type paper machines. The latter employ cylinders covered with fine mesh wire to extract pulp from the slurry stock onto the surface. The material is then deposited in thin layers (one from each cylinder) to form the wet web. After all the cylinders have deposited their contribution of fibers, the wet web of paper is pressed to remove excessive water. Each pair of press rolls gradually increases the pressure until the wet web is dry enough and strong enough to support its own weight when it leaves the press section.

The Fourdrinier machine employs a long wire belt for formation of the wet web. Paper stock is fed onto the moving wire through a sluice from

a headbox, and, in contrast with a cylinder machine, the web is made up as a contiguous single layer. Over a relatively short distance enough water drains through the wire by gravity and by passing over suction boxes that the mat can leave the wire and pass onto a felt where pressing begins.

All machines employ a long section of many steam heated cylindrical dryers. As the sheet leaves the wet end after all possible moisture has been removed by mechanical pressing, the remaining excess moisture must be removed by evaporation. The sheet of paper passes over all of these dryers which eventually produces a dry sheet to customer specifications.

The last step in the actual paper manufacturing is calendering or pressing for the purpose of obtaining a uniform finish and thickness. Also at this station it is possible to apply surface sizing or other forms of coating or stain.

After passing through the calenders the paper is wound onto reels to be rewound and trimmed to meet size orders. If the customer wants his paper in flat sheets, it is run directly from the paper machine through a sheeter. In either case, when the paper is finished it is banded, wrapped, labeled, and weighed.

A substantial amount of the total production of Plant A is sent to a converting plant for further processing. Most of this processing consists of slitting wide rolls into narrow widths to be used for winding into cores and tubes. This plant also performs cutting from rolls into sheets, precision trimming of sheets, and laminating.

I-3.2 Plant B - 90 Percent Recycled Raw Material

General Description

This plant is a major manufacturer of tissue items, producing 800 tons of facial tissue, toilet paper, napkins and paper towels per day. Approximately 90 percent of the raw material required is supplied by waste paper, which is a slightly higher percentage than most other tissue mills.

Plant personnel supplied a report on PCBs generated by them in 1975. The concern for effluent water quality dates back to the establishment of a primary treatment system in conjunction with the start-up of a deinking process in the 1930's. The secondary treatment system was put into operation several years ago, prior to the regulations governing suspended solids. A tertiary process is in the development stage at the present time. PCB measurements were begun in-house during 1975. Data on PCBs content of products prior to 1975 have been obtained and are reported elsewhere.

Characterization of Raw Material

Although most of the raw material for this plant is wastepaper, less than 50 percent of this is classed as post-consumer waste; in other words, most of the returning paper stock has never been previously recycled. Office wastepapers of the ledger grades are removed from the incoming stock, but a quantitative screening of all returning paper stock is impossible from an economic standpoint. As shown by industry data and the modeling effort in this report, even a few sheets of the carbonless copy paper can have an observable affect on PCB concentrations in a single day's output.

Office wastes in general do not make a desirable paper stock, since many office paper products contain binders, colorants or other minerals that are difficult to remove and cause problems in the papermaking process. These wastes are purchased by the mill primarily to assist their paper dealers. They do become more important during periods of short paper stock supply.

Effluent PCB Levels

PCB concentrations in clarified mill intake water were less than 0.1 ppb. Measurements of deinking, mill and combined effluents were reported to range from 0.3 to 2.7 ppb.

In-Plant Vaporization Estimate

The plant has performed a water mass balance on its paper machines. An average of 570 gal. per ton of product was lost. Assuming the production of 800 tons per day and a water concentration of PCBs (excluding

PCBs bound to fines and assumed not to evaporate) of 0.1 ppb, evaporative losses would be 0.00038 pounds of PCB per day or less than 0.15 lbs/year. This is probably an undetectable loss if direct measurement was attempted.

I-3.3 Plant C - 80 Percent Recycled Raw Material

Pulp Generation

Pulping is a batch process at this plant. Wastepaper, accounting for about 80 percent of the raw material, is added to pulpers #3 and #4 together with hot water and caustic soda. Steam jets raise the temperature to about 185°F and deinking continues for about 1.5 hours. After deinking, the stock from both pulpers are dumped together yielding a stock slurry of about 7 percent consistency. From here the stock is passed through a one inch bar screen that removes large contaminants such as string and rags. The pulp is now pumped to a holding chest.

Manually operated valves determine the quantity of stock discharged from the holding chests through two 1/8-inch screens. The accepts here have a concentration of about 4.5 percent, and rejects from the screens are trucked to a landfill. Accepts are stored in another holding tank.

Upon leaving this tank, the stock is diluted to about 0.7 percent solids and run through centrifugal cleaning to remove fine contaminants. Accepted stock is now directed to a screen with 0.010 inch slots. Accepted stock from this screen pumped to two slope washers that have counter-stock flow of water. These washers are arranged in series with the second one increasing the stock consistency (solids concentration) to about 5 percent.

At this point the stock is pumped to two washers set up in parallel. The washed stock, with a consistency of about 2 percent solids, is pumped to a storage tank until the chlorination tank is ready for a new batch. Water for the washers comes from the slope washers.

During chlorination, chlorine gas is pumped into a tank holding the stock and allowed approximately five minutes retention to react. The stock batch is then pumped towards a vacuum washer. However, before it is washed, sodium hydroxide is added which reacts with any residual chlorine to form

sodium hypochlorite to augment the bleaching process; the final pH is 9. The bleached stock is sent to retention tanks.

The stock pulp is sent to a vacuum washer to remove materials made soluble by chlorination. This wash water originates from the paper machine water supply, the white water. The filtrate from the washing process is pumped to the slope washers which conditions the new batch for chlorination by reclaiming the chemicals and also reduces the amount of water used. The stock pulp now has a consistency of about 5.5 percent. Upon leaving the washers, the stock pulp is pumped to high density storage tanks to await the papermaking operation.

This mill also has a separate pulping system for virgin pulp and pulp substitute. However, both virgin and substitute pulp are blended with the wastepaper stock pulp. Here, chemicals are added to develop better fiber bonding strength.

Papermaking

From the storage tanks the stock pulp is diluted to about a 0.3 percent consistency and pumped to the headbox. Prior to entering the headbox, the pulp is rewashed, rescreened and run through a three stage centrifugal cleaning system. Much of the water used in papermaking is recycled. Excess white water is stored to be utilized in various operations in the mill.

The sheet is pulled through on a felt belt and dried. The speed that it is pulled through regulates the strength of the product. Thickness is governed by this speed and by slicing the sheet off the belt with a doctor blade. Several plies are then rolled together to produce a paper of desired specifications.

Water Source and Effluent Treatment

Plant C uses municipal water which is believed to be relatively low in PCBs. The intake volume is about 1.5 million gallons per day.

The discharges from Plant C enter a wet well from which the wastewater is screened and sent to a company-operated treatment plant.

Treatment consists of primary clarification and a two-stage activated sludge system. The treatment plant effluent is discharged to the Fox River (mid-stream).

I-3.4 Plant D - 50 Percent Recycled Raw Material

Plant D is a major recycling operation. Six grades of wastepaper (e.g., office and foodboard) are the major constituents of the raw materials utilized to produce acceptable deinked pulp stock. This accounts for approximately 50 percent of the required pulp with the remaining being composed of purchased virgin pulp and pulp substitute. There are essentially two pulping systems - one for wastepaper and deinking and the other for the virgin and substitute pulp.

Pulping and Fiber Recovery

Here, wastepaper is mechanically broken down with hot water (about 190°F), caustic soda, surfactants and deinking chemicals by means of a ribbed rotor at the bottom of the hydropulper. Much of the heavy waste such as metallic objects and plastic sheets are collected in traps at the bottom of the pulper. At this point, the pulp stock has about a 6 percent consistency (consistency being the percent solids to liquid).

The deinked pulp leaves the hydropulper through perforated plates and is pumped to blending chests for additional retention time and agitation. The pulp now has about a 2.5 percent consistency. Upon leaving the chests, the pulp is passed over a filter that recovers the cooking liquor in the filtrate. The filtrate is reused in the pulper to recover the heat and residual chemicals. Excess washer water is reused for other operation dilutions. Water is extensively recycled in the deinking operation.

The pulp is now sent to centrifflers, which are centrifugal cleaning devices for removal of pins, staples, and other heavy particles. The accepted pulp has a 2 percent consistency and it is sent to a centrisorter pressure screen. Accepted stock from the pressure screen goes on to washing while rejects are passed through a deflaker and then across a screen for further fiber recovery.

The pulp then enters a four-stage counter-flow washing system. The first stage consists of 2 cylinder washers, the second and third stages consist of sidehill washers, and the fourth is another cylinder washer. The cleanest water is used for dilution at the fourth stage and the filtrate is fed to the preceeding (third) stage. This filtrate is then used in the second stage and its filtrate in the first stage, where the filtrate is discharged to waste treatment. The water in the washing process originates from the discharge of the paper machine water, white water, and the acid and alkaline bleaching water.

Following washing, the stock is bleached with chlorine, followed by treatment with caustic and then hypochlorite. The next treatment is a three-stage pressure screen system. Accepted stock pulp from the first stage pressure screen then goes to a five-stage centrifugal cleaner system for removal of small heavy contaminants such as ink. Those fibers rejected are replaced in the centrifugation scheme to concentrate the contaminants and unacceptable pulp, and to reclaim as much of the shunted acceptable pulp as possible. Following this is a four-stage system of centrifugal reverse cleaners for removal of lightweight contaminants such as plastic fibers and adhesives. After the cleaning system the stock goes to the final washer for thickening and storage in high-density towers. The water removed by the thickening process is reused in other washings and in the bleachery.

The above description for secondary pulp supplies 50 percent of the materials required to meet the current demand of Plant D. The remainder is composed of purchased virgin pulp and pulp substitute. Both are warehoused in solid form and repulped in their respective hydropulper, using recycled paper machine white water. This pulp is then pumped to storage chests until needed. From here, the pulp is sent to refiners for fiber shortening and fibrillation to enhance greater bonding capacity.

From the refiners the pulp is discharged into a pipeline that contains the secondary pulp for blending of the types. After sufficient time to ensure homogeneity, components such as clay, titanium dioxide and alum, to name a few, are added to the stock pulp as it moves to the paper machine.

Papermaking

Stock taken from the high density storage tanks is diluted and pumped to the papermaking system. Here the stock volume is controlled to insure a constant head level. By operating under a known head, the texture of the pulp sheet falling on the Fourdrinier remains the same throughout the operation.

The endless mesh belt of the Fourdrinier effectively drains enough water from the pulp slurry to permit the fibers to make a sheet called the wet web. Much water is recycled during papermaking operations. Since this water is falling from the bleached product, the pulp imparts a white color on the water and hence is called white water. Because water is continually being added here, there is an excess overflow. This surplus water is stored and used to supplement the water diluting the deinked stock. Several hundred thousand gallons of water escape each day due to evaporation while the paper is being pressed and dried. When the pulp leaves the headbox, it is 99 percent water; after passing through the presses, it is about 60 percent water, and after the driers, only about 5 percent moisture remains. This is the percent moisture of the rolled product.

Intake Water and Wastewater Treatment

Since the product color and composition is highly important, the water used throughout the operations necessarily should not contain any suspended contaminants that are able to be removed. Therefore, this mill has a treatment facility for intake water, utilizing flocculation with alum and lime, addition of algacide, and filtration. The filter is composed of the following: top layer - 8 inches of coal; middle layer - 2 feet of sand; bottom layer - 2 feet of crushed stone.

Currently, this mill only has primary treatment, a clarifier. The present system has about 90 percent SS removal but only about 25-30 percent OBD reduction. The effluent from this clarifier is being discharged to the Fox River. The average flow for 1975 was 3.9 MGD. This volume can be broken down as follows:

- 2.5 MGD from deinking
- .9 MGD from papermaking
- .3 MGD from water plant
- .2 MGD disposal plant and misc.

Under construction now at Plant D is a 2-stage activated sludge system. Preliminary investigations on this type of treatment facility for pulp and paper wastewater discharges indicates that this system is very effective at further reducing the SS levels and greatly reducing effluent BOD.

Clarifier sludge contains 10 percent solids and is further consolidated in compaction tanks to a 12 percent solids level. The sludge is furthered dewatered to 28 percent solids by lime addition and subsequent vacuum filtering. The filtrate is returned to the primary clarifier and the dewatered sludge is trucked to their private landfill.

Landfill Operations

The company has opened a new landfill which covers about 18 acres. Preliminary geologic investigations revealed a solid bedrock foundation. The area is encompassed by a man-made compacted clay dike, effectively eliminating any surface runoff from the landfill.

Concern for groundwater contamination resulted in the construction of monitoring wells. There appears to be two layers of groundwater separated by a clay table. When completely filled, the landfill will be slightly dome shaped with a 2 degree slope.

I-3.5 Plant E - Less Than 50 Percent Recycled Raw Material

General Description

Plant E is basically self-contained, i.e., it produces in-house nearly 50 percent of their fiber requirement by chemi-mechanical treatment on hardwoods. The remaining 50 percent is composed of purchased bleached kraft pulp from Canada and other U. S. sites and such items as foodboard, cups, and IBM cards. No carbonless paper is utilized. Production is between 300 and 400 tons per day.

Product PCB levels from Plant E have consistently remained below 5 ppm proscribed by FDA. Effluent levels of PCBs are also apparently lower than most of the industry using reclaimed fiber, probably because of efficient removal of suspended solids in the waste treatment systems.

Pulping

Plant E uses chemi-mechanical pulping, virgin pulp from purchased bleached kraft pulp, and secondary pulp from wastepaper. Each operation occurs in a specific pulper and the stock is blended later according to product specifications. The virgin pulp slurry is generated by only adding hot water while the secondary pulp requires hot water plus caustic soda plus hypochlorite bleaching powder. Both virgin and secondary stock pulp are not stored but directly mixed with the chemi-mechanical pulp stream. Plant E is a continuous operation, and all grades of pulp are being used simultaneously but only that from the chemi-mechanical system is allowed a detention.

Blending of pulp grades occurs in machine chests, each having a different percentage of the grades depending on the eventual product. It is just prior to these chests that other additives such as clay and other fillers are added to provide the required paper characteristics.

Papermaking

Each pulp stream is passed through similar machines, with all machines having an additional coating step. The stock pulp enters the Fourdriner to produce the wet web, approximately 19 percent of the water content is voided here (in other words the web's consistency increases from 0.5 to about 20 percent). The wet web is then drawn through a series of presses to further remove the water. The majority of the remaining moisture is removed by drawing the sheet through a series of dryers. Final moisture is about four percent.

Following the drying operation, the sheet is passed through rollers to smooth it and produce a uniform thickness. It is then rolled, trimmed, cut and warehoused. Some cut rolls are sent directly to a specification cutting section for high-demand dimension consumer products (a sizeable fraction of the total production is used for telephone books).

Waste Treatment

This plant utilizes two waste facilities; a fluidized bed incineration for spent liquor in the pulp mill operation, and a wastewater treatment plant for water used in the papermaking process plus excess wash water and associated solids from the pulp mill.

The chemi-mechanical pulp mill effluent with a 6 percent solids content is sent to an evaporator where the solids content is increased to about 45 percent. The liquor, now a syrup, is placed in the incinerator operating at approximately 1300°F, and the remaining moisture is flashed off allowing the organics to be volatilized. At the bottom of the unit, air jets keep the ash in motion (fluidized). Therefore, pulp mill activity is a closed system with no effluent, and the excess ash is trucked to a landfill.

Wastewater currently receives only primary treatment in two parallel clarifiers, but removal of approximately 96 - 98 percent of the suspended solids is achieved with 40 - 50 percent BOD removal. A new secondary treatment system will begin operations in the near future. Overflows from the clarifiers will be combined and discharged to the secondary treatment reactor, which is a closed, oxygenated, three-segment tank. Effluent from the reactor is then sent to a settling tank and after a determined retention time the supernatant liquid is discharged to the Fox River. The new system is designed to handle 6.5 mgd with a three hour retention. The mill has recently reduced its water requirement from 8 mgd to 6.8 mgd in preparation for the secondary system.

The sludge will be removed with some of it reused as seed in the oxygenated reactor tank while most of it will be dewatered to about 22 percent solids by a vacuum filter. This waste sludge is presently deposited on a landfill. There is no monitoring for groundwater contamination at this time.

Management is currently communicating with other mills that may be able to use their sludge as it contains a high fiber concentration that can be used for other paper products.

I-3.6 Crown Zellerbach Research Laboratory and Camas Mill

A meeting with Dr. Herman R. Amberg, Director of Environmental Services for Crown Zellerbach and members of his staff was held on June 29, 1976, at the Central Research Division in Camas, Washington. Crown Zellerbach has a number of mills which range from total use of virgin fiber to complete dependence on secondary fiber. Since most chemical analyses are done at the Central Research location, it was felt that the question of analytical accuracy could be de-emphasized and relative differences in PCB concentrations assessed.

CZ analytical detection limits for PCBs in paper were routinely 1 ppm and are apparently dropping under continued attention to details of the analysis. Some data had been taken as far back as 1971. A number of important points were discussed:

- 1) No measurable PCBs had been found in virgin wood.
- 2) Exhaustive sampling and analysis had failed to identify any PCB generation during the pulp bleaching stages.
- 3) Process chemicals were surveyed to identify any sources of PCB and none were found.
- 4) Data would be made available through API.

A tour of the Camas Mill, which makes specialty papers, was taken. This mill used virgin pulp, a small amount of purchased pulp, sawdust and wood chips from surrounding sawmills as its raw material. Inputs of PCB were therefore limited to that occurring in the intake water.

I-3.7 Weyerhaeuser Company

On June 25, 1976, Dave Morris and Ted Ross of the Weyerhaeuser Corporate Engineering Department at Tacoma, Washington met with a Versar representative. Mr. Ross had previously been involved with EPA contract work which related to effluent guidelines for the pulp and paper industry and both were following PCB-related matters.

Weyerhaeuser's papermaking operations are based on a 100 percent virgin fiber raw material. As a result, it was believed that this mill would only encounter PCBs that were associated with the intake water, or as a result of internal PCB uses in transformers or capacitors. Contingency spill plans were set up in every mill; transformers containing PCBs were diked and monitored for any signs of leakage.

1.0 EXECUTIVE SUMMARY

1.1 Historical Background

In 1966, Soren Jensen reported the presence of PCBs (polychlorinated biphenyls) in Swedish fish and wildlife as a result of a study begun in 1964. The Food and Drug Administration began, in 1967, a program to develop analytical techniques for PCBs. During this period concern about PCBs in food and in the environment of the United States was increasing. In 1969, FDA alerted its Districts to expect PCBs in food samples, and to analyze for PCBs in foods sampled for pesticide analysis. Findings of PCBs in fish, milk, eggs, and poultry samples occurred throughout 1969 and 1970.

In August, 1971, a significant level of PCBs was found in a grain and cereal composite of a Market Basket sample by FDA in their Total Diet Studies, and the contamination was traced to the greyboard packaging of a cereal. According to FDA (supporting data for Press Briefing by Dr. C. C. Edwards, September 29, 1971), the highest PCBs level found in greyboard was 433 ppm. FDA met separately with the American Paper Institute and with food manufacturers in September, 1971 to inform them of the PCBs problem in foodboard and to discuss approaches to its solution.

By the end of September, 1971, all concerned parties appear to have agreed that the major source of greyboard contamination was recycled carbonless copy paper which was known to contain PCBs. Production of this material had ceased as of June 1, 1971, but recycling was continuing. In the same time frame, Monsanto Industrial Chemicals Co., essentially the sole U.S. producer of PCBs, announced cessation of sales for all but closed electrical systems (capacitors and transformers) applications.

On July 6, 1973, the FDA issued its final rule-making document on tolerance levels of PCBs in various foods and paper food-packaging material (10 ppm for paper food-packaging). By this time the paper industry had succeeded in reducing PCB levels in food-packaging materials made wholly or partially from recycled fiber to well below the FDA tolerance limit. This appears to have been accomplished through more judicious selection of recycled fiber for foodboard manufacture, including:

- (1) Cessation of use of cutting scrap from office form production (where carbonless copy paper content could be very high); and
- (2) Limitation or selectivity in the use of office waste for foodboard production.

Levels of PCBs in foodboard have generally continued to decline since 1973 to a current level of less than one ppm, except for occasional "hot spots" resulting in levels of up to five ppm. These "hot spots" are generally attributed to the inclusion of significant quantities of outdated office files containing carbonless copy paper. PCB levels in other paper products are also in the one ppm or below range; those made from virgin pulp, of course, exhibit by far the lowest PCB levels.

1.2 Carbonless Copy Paper

Aroclor 1242, a mixture of PCBs containing an average of 42 per cent chlorine, was purchased from Monsanto and used in carbonless copy paper as an ink carrier or solvent during the period 1957-1971. The total amount used for this purpose was 44,162,000 pounds, approximately 28 per cent of the total estimated Monsanto sales for plasticizer applications and 6.3 per cent of Monsanto domestic sales of PCBs during 1957-1971. The average content of Aroclor 1242 in the carbonless copy paper was 3.4 per cent.

The National Cash Register Company (NCR) was the developer and sole marketer of the PCB-containing carbonless paper, although Appleton Coated Paper Co., Appleton, Wisconsin; Mead Corp., Dayton, Ohio; Combined Paper Mills, Combined Locks, Wisconsin; and Nekoosa-Edwards Paper Co., Port Edwards, Wisconsin, at one time or other performed the actual production under license from NCR.

The Aroclor 1242 was used as a solvent for certain color reactants which were encapsulated into microspheres producing aggregates 10-20 microns in diameter and applied to one side of the paper during the coating process. The walls of the microspheres were an aldehyde-hardened gelatin-gum arabic formulation which ruptured and released the dye under application of local high pressures as from pens or pencils. In 1971 alkyl-biphenyls were used as the dye carrier in place of Aroclor 1242.

It should be noted here that PCBs, primarily Aroclor 1254, were used to a limited extent in printing inks. The total usage in this application is estimated at 50,000 pounds, primarily in the 1968-71 time frame. No other actual or potential usage of PCBs in paper product or usage besides the copy paper and these inks has been definitely identified to date.

1.3 PCBs in Paper Mill Effluents

It has been recognized for several years that effluents from paper mills contain environmentally significant quantities of PCBs. The PCBs in these wastewater streams are generally more similar to Aroclor 1242 than to any of the other Aroclors or to PCBs found in the general environment and biota (which tend to exhibit chromatographic fingerprints corresponding to higher chlorine contents than 1242). Thus, although introduction of PCBs into paper-making processes through process water usage undoubtedly occurs (PCB levels at water intakes of paper mills average about 0.1 ppb), the major source of process contamination by PCBs appears to be carbonless copy paper contained in recycled wastepaper.

A number of paper mills, in response to the need for improvement of water quality, have installed or are now installing waste treatment processes which are expected to greatly reduce the PCB levels in their effluents. However, these levels may still be typically above the one ppb level proposed by EPA on July 23, 1976 as an effluent standard for capacitor and transformer manufacturers, and the quantities of wastewater from paper mills are generally much larger than from such equipment manufacture. In addition, sludges or concentrates from paper mill water treatment may be sufficiently high in PCBs as to warrant concern about proper disposal.

The magnitude of the PCB control problem is illustrated by the existence of 230 paper mills producing pulp completely derived from recycled wastepaper and 550 other facilities utilizing some fraction of secondary fiber in their pulp production (typically 10 to 15 per cent). Recycled wastepaper amounts to about 13 million tons per year as a pulp source, third in importance to pulpwood and forest product wastes.

On-site measurements and laboratory experiments have shown the PCB to be substantive to fiber; that is, preferentially associated with the fibers rather than the water in which they are carried. Highest PCB concentrations in fiber slurries are associated with the smallest fiber particles, the "fines". Economical utilization of the fiber requires it to be exhaustively recycled in attempts to associate it with the paper being manufactured. Fines control porosity, surface finish and affect brightness of the product. Discharge of PCB from a typical mill thus appears to be primarily by way of the suspended solids. Removal of suspended solids accomplishes PCB removal, and a consideration of the high surface to volume ratio of the smaller particles shows why they are the ones that need to be removed for a low PCB effluent.

A continued trend of increased water recycling is exhibited by the industry, for the purpose of minimizing external treatment costs as well as recovering chemicals, heat and raw material from process streams. This has culminated in the design and construction of a totally process-effluent free bleached kraft pulping mill in Canada. Only non-contact cooling water will be discharged. New end-of-pipe treatment systems, such as the Zurn-Attisholz 2-stage activated sludge system installed by Wisconsin Tissue Mills, offer promise of significant reductions in BOD and suspended solids/PCBs. Cost estimates for carbon absorption treatment (end-of-pipe) range from \$886 to \$1227 per pound of PCB removed.

Some data exists to show net removal of PCB from an intake water as evidenced by a lower concentration in the effluent. The paper-making process in such a case is withdrawing the PCBs from the environment and stabilizing them in the much less mobile paper phase. Of course, numerous routes whereby these PCBs can become remobilized (in air or water) are available.

It is believed that essentially all of the Aroclor 1242 used in carbonless copy paper has been released to the environment (assuming negligible degradation). At the present time more than half can be attributed to landfills and the remainder dissipated. In a sense, these PCBs were mobilized upon the initial production of the paper, and their passage through paper mills merely resulted in partition between the accepting media (water, air, solid wastes, products).

2.0 PROCESS TECHNOLOGY OF THE PULP AND PAPER INDUSTRY

2.1 Background

Pulp and paper manufacturing consists of two distinct processes. Pulping is the reduction of whole wood or waste paper into a semi-liquid fibrous mass, while papermaking consists of forming discrete fibers into paper sheet or paperboard. There can also be ancillary operations which provide special features such as coloring, coating and backing.

The processes require four basic raw materials: fiber, water, energy and chemicals. In contrast to the earliest mills, newer mills may be located some distance from their fiber source, especially in the case of recycling-oriented mills where proximity to fiber means an urban center rather than a forest. The water requirement is definitely being reduced in magnitude as recycling methods are being developed within the industry. The recycling has the benefit of assisting in meeting more stringent discharge criteria as well as recovering chemicals from process waters and meeting energy needs by recovering energy from organic wastes.

The wood used in pulp and paper manufacturing is called pulpwood. It can be either hardwood from deciduous broad leaf trees, or softwood from coniferous or needlebearing trees. This categorization reflects the proportion of cellulose to lignin (the substance which holds the fibers together). The supply arrives at the pulping facility as logs, chips made from roundwood, as sawdust, slab or chip residues from saw mills.

In traditional logging practice, the central portion of the tree was utilized in the pulping mill requiring a removal of the bark from the log. Mechanical debarking or hydraulic means are used with the bark often collected and burned as an energy source.

2.2 General Pulping Techniques

Regardless of the type of process involved, the basic objective of pulping is to reduce the wood to non-woody fibrous materials by rupturing the bonds between the fibers of wood. This task entails either cooking the pulpwood (using suitable chemicals) in a digester under controlled conditions of

time, temperature, and pressure or reducing the wood to fibers by mechanical or semichemical means.

2.2.1 Mechanical Pulping

Mechanical pulping, sometimes called "the groundwood process," operates by mechanical means, generally using either a large grindstone or a machine called a "refiner". The present methods of manufacture do not differ in principle from that of 1867, though the size, capacity and form of the grinders have undergone much change. In all equipment the logs of wood are pressed against the face of a rapidly revolving grindstone in such a way that the length of the log is parallel to the shaft holding the stone. In the older grinders, logs two feet long were placed by hand in pockets attached to the grinder frame, and were forced against the stone by pressure plates operated hydraulically. Usually there were three pockets on each stone so that one could be opened, filled with wood, and put back into operation without shutting down the entire grinder.

Modern grinder installations are very different in appearance from these old ones, and operate much more efficiently. Continuous magazine grinders have been developed, in which the logs are fed into the grinder on one floor and dropped down through the magazine to the pockets of the grinder on the floor below. Such grinders are usually installed in pairs driven by a motor which may rate as high as 4000 horse power and have a turning speed from 3,500 to 5,000 rpm.

The increasingly popular disk mill method uses a refiner to shred and grind groundwood chips between counter-rotating metal shearing disks. Refiner-ground wood, which usually has longer fibers, is preferred over stoneground wood since it yields a stronger paper.

Both types of mechanical pulpers are generally used in an integrated papermaking facility, in which the resultant fiber is thickened by removal of water and stored as slush pulp rather than being formed into flat sheets for sale as market pulp. Characteristically, groundwood pulping requires high power - over 32,000 kw to operate a 500 ton per day groundwood mill.

Unlike chemical pulping, groundwood pulping entails considerable fiber damage. It produces a relatively weak paper that discolors easily on exposure to light. On the other hand, groundwood processes have the advantage of converting about 95 percent of the dry weight of wood into pulp, compared to about 50 percent for chemical processes. The strength problem may be overcome by adding long-fibered chemical pulp to groundwood pulp between the pulping and papermaking stages.

Groundwood pulp constitutes 70 to 80 percent of newsprint by weight. Groundwood plants are principally located in Canada and the southern U.S., where the supply of softwood and electricity is ample.

2.2.2 Chemical Pulping

Chemical pulping is the process of cooking wood with suitable chemical reagents to dissolve and degrade the lignin, the cementing material between the wood fibers, and allow the fibers to be easily separated. The diversity of pulping processes is increasing in response to the availability of improved technology, the need to improve productivity, and the requirement to curb pollution. Currently, two major chemical techniques and one semichemical technique of widespread commercial importance are employed.

The most significant chemical processes are the sulfate or kraft process, the acid sulfite process, and the neutral sulfite process. In the kraft and the acid sulfite processes, the debarked and chipped wood is loaded into a large metal digester along with the appropriate chemicals in an aqueous solution. Heat is applied and cooking is continued, usually at high temperatures and pressures, until the desired degree of delignification and purification is obtained. Cooking transforms lignin, some carbohydrates, resins, and mineral matter into soluble compounds that can be removed by washing. For most pulp grades, over 95 percent of the lignin is eliminated. Because the cooking liquid also attacks and removes some desirable hemicellulose and cellulose from the wood, relatively poor yields are inherent in chemical pulping.

The type of process and products involved determines the necessary cooking conditions. The important variables are the size and physical properties

of the chips, the liquor composition and concentration, and the time, pressure, and temperature of cooking. The liquor concentration is the most important variable since it affects the reaction rate and cooking time; a large initial concentration increases the reaction rate but decreases the yield since the stronger liquor removes or weakens more of the desirable cellulosic materials. From an economic standpoint, the most important variables in cooking are the chemical composition and the thermal energy requirement. The industry is concentrating on improved methods of recovering and recycling the chemicals and of reducing energy inputs.

The acid sulfite process, discovered in 1874 and well established commercially by 1890, remained the most important chemical process until it was overtaken by the kraft process in 1937. Here, the cooking liquor is made at the mill by burning sulfur in air to form sulfur dioxide and reacting the gas with limestone to produce a cooking acid of the desired composition and concentration.

For years the only base used was inexpensive calcium, but sodium, magnesium, and ammonia-based sulfite liquors have come into use recently, especially in Scandinavia and North America, for various reasons: reduced cooking time, easier recovery of cooking chemicals, reduced stream pollution, more marketable by-products, fewer required screenings subsequent to cooking, and greater brightness. However, the soluble bases other than calcium cost four to five times more per ton of pulp and their advantages in yield, reduced cooking time, and improved pulp quality alone, without the possibility of spent liquor recovery and before the advent of stringent pollution controls, would not have warranted industry use.

Since the spent liquor in the calcium-based process is uneconomical to recover and presents a major water pollution control problem, most plants will abandon the process unless an economical way can be found to recover or dispose of the spent liquor. Spent liquor has been variously used, e.g., as a road binder or in the manufacture of yeast, vanilla, alcohol, fertilizers, insecticides, tanning agents, and inks. It can also be burned in concentrated form to produce power and steam; the heat value of the dried sulfite waste is about two-thirds that of industrial coal, but much of the energy produced must be used to evaporate and con-

centrate the liquor in preparation for burning. Even this limited recovery is likely to become more attractive as energy prices rise.

Despite such efforts to find alternative uses for the spent liquor, most mills have continued to dispose of it as a waste product. Recent water pollution control requirements might alter this trend.

The kraft (sometimes called the sulfate) process is now predominantly used in pulping. The name "sulfate" (derived from the sodium sulfate used as the make-up chemical in the chemical recovery process) is misleading since the active cooking agents are mostly sodium hydroxide and sulfide.

As in the sulfite process, wood in chip form is cooked in large steel digesters in the presence of a cooking liquor and under conditions of elevated temperatures and pressures. The cooked chips are then defiberized in a blow tank and screened as necessary before washing and bleaching. The prepared pulp may be either pressed and dried into flat sheets for sale or shipment to another facility or retained in a slurry form for use at an adjoining paper or paperboard plant.

The kraft process has various advantages: it can be used on almost any species or quality of wood; its cooking times are short; it entails no pitch problems; recovery of the spent liquor is relatively easy; and it yields valuable by-products. The pulp produced has great strength and can be bleached to high levels of brightness. The efficient chemical recovery system is especially advantageous and economical since the sodium hydroxide used in the kraft process is a very effective but relatively expensive chemical.

The principal disadvantages of the process are its high capital costs, high cost of bleaching, and discharge of several highly malodorous waste gases (e.g., hydrogen sulfide). Regulations requiring controlled discharge are thus significantly affecting the economics of the kraft process. Electrostatic precipitators and scrubbers are being used to reduce odor by precipitating dust particles to which the odor producing particles cling. Unfortunately, since the wastewater from these cleaning operations cannot be used for pulp washing because the odor is imparted to the pulp, this deodorizing method merely substitutes a liquid waste problem for a gaseous one.

2.2.3 Semichemical Pulping

Semichemical pulping, which combines mechanical and chemical pulping features, chemically treats the wood to achieve partial softening and then uses mechanical refining to complete the fiberization. Semichemical pulping offers several advantages over both chemical and groundwood processes. The yield is from 65 to 90 percent of the weight of the wood because only part of the lignin and hemicellulose is removed. This is considerably better than the straight chemical process. The chemical pretreatment reduces the amount of power necessary for the subsequent mechanical reduction, increases the average fiber length, and enables the process to be used effectively with hardwoods. In addition, since semichemical pulping uses fewer chemicals than the pure chemical processes and requires a lower capital investment, it lends itself to use in smaller plants. One drawback is that semichemical pulping only works well for hardwood and is not used for softwood species.

The two most important types of semichemical pulping are the neutral sulfite semichemical and the cold caustic processes. The more widely used neutral sulfite process treats the wood with a solution of sodium sulfite which, during cooking, is buffered to about pH 7 with a buffering agent such as sodium bicarbonate. The physical characteristics of the neutral sulfite process pulp make it particularly well suited for use as a corrugating medium. The neutral solution produces a pulp with high yield, about 65-80 percent, strength, and brightness without offensive odors.

The cold caustic process, which employs caustic soda (sodium hydroxide) to produce coarse pulps for corrugating and some finer pulps for printing papers, is particularly useful with high density hardwoods that cannot be used in the groundwood process. Efficient use of chemicals and reduction of the mechanical energy required for subsequent refining make this process lower in operating costs than either groundwood or other semichemical processes. The pulps produced are inferior to kraft pulps in physical properties but stronger than or equal to groundwood pulps made from softwoods.

Chemical recovery in semichemical mills, unlike in the kraft system, can use a number of chemical processes. For the semichemical process

using caustic soda, a recovery process similar to that used to recover sodium hydroxide in the Kraft process may be used. Most of the remaining techniques involve either combustion or cross-recovery (using the kraft mill recovery system).

2.2.4 Secondary Fiber Pulping

Secondary fiber, derived from wastepaper, is a principal source of pulp for some papermaking facilities around the large metropolitan areas. Secondary fiber accounts for about 20% of the fiber used for pulp today. Although the rising cost of fiber will undoubtedly induce the industry to increase use of secondary fiber (especially recycled paper, the highest-quality wastepaper used for making pulp today), such increases may be less than is popularly anticipated. Rising energy costs, the difficulty of separating wastepaper from other trash, and the lack of captive supplies may limit the growth in use of wastepaper as a fiber source. Mills that use wastepaper generally have little control over their secondary fiber supply, although firms are increasingly seeking long-term wastepaper supply arrangements.

2.2.5 Dissolving and Special Pulps

Variations of the basic sulfate and sulfite processes which produce pulps for paper and paperboard are used to produce a special type of pulp called dissolving pulp. This segment of the pulp industry has become so specialized that it operates much as a separate industry. To generate dissolving pulp, pulps produced by kraft or sulfite processes are chemically purified to remove all semi-cellulose and to extract pure cellulose. The pure cellulose is then used as a raw material to produce rayon, cellophane, and cellulose derivatives used in such diverse products as explosives, detergents, lacquer, food product thickeners, hand lotions, and automobile accessories. Dissolving pulp is also used to make glassine paper (the paper that forms the clear window in window envelopes). Dissolving pulp facilities are frequently located adjacent to kraft and sulfite mills so that the pulp can be delivered in slush form without drying.

2.3 EPA Classification of Mills by Pulping Method

It is at the pulping stage that the process schemes allow for differentiation between plants. In compliance with certain sections of FWPCA of 1972, EPA has established the following sub-categories of pulp, paper and paperboard operations for the purpose of establishing effluent guidelines:*

Table 2-1 EPA Mill Classification

1. Bleached Kraft: Dissolving Pulp
2. Bleached Kraft: Market Pulp
3. Bleached Kraft: Fine Papers
4. Bleached Kraft: B.C.T. Papers
5. Papergrade Sulfite
6. Papergrade Sulfite Market Pulp
7. Low Alpha Dissolving Sulfite Pulp
8. High Alpha Dissolving Sulfite Pulp
9. Soda
10. Groundwood: Chemi-mechanical (CMP)
11. Groundwood: Thermo-mechanical (TMP)
12. Groundwood: Fine Papers
13. Groundwood: C.M.N. Papers
14. Deink
15. Non-Integrated Fine Papers
16. Non-Integrated Tissue Papers
17. Non-Integrated Tissue Papers (fwp)

EPA defines each class of mill as follows:

1. BLEACHED KRAFT: DISSOLVING PULP means that production of a highly bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. Included in the manufacturing process is a "pre-cook" operation termed prehydrolysis. The principal product made by mills in this subcategory is a highly bleached and purified dissolving pulp which is used principally for the manufacture of rayon and other products requiring the virtual absence of lignin and a very high alpha cellulose content.

* Reference No. 1; further industry and process descriptions, including wastewater characterization, can also be found in this and associated references.

2. BLEACHED KRAFT: MARKET PULP means the production of bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. Included in this subcategory are mills producing papergrade market pulp as the only product.
3. BLEACHED KRAFT: FINE PAPERS means the production by integrated pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. The principal products made by mills in this subcategory are fine papers which include business, writing, and printing papers.
4. BLEACHED KRAFT: B.C.T. PAPERS means the production by integrated pulp and paper mills of bleached pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. The principal products made by mills in this subcategory are papers of low filler content including paperboard (B), coarse papers (C), and tissue papers (T).
5. PAPERGRADE SULFITE means the production by integrated pulp and paper mills of pulp and paper, usually bleached, by a "full cook" process using an acidic cooking liquor of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The principal products made by mills in this subcategory are tissue and fine papers.
6. PAPERGRADE SULFITE MARKET PULP means the production of pulp, usually bleached, by a "full cook" process using an acidic cooking liquor of sulfite of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The principal product made by mills in this subcategory is papergrade market pulp.
7. LOW ALPHA DISSOLVING SULFITE PULP means the production of highly bleached and purified pulp by a "full cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide. The pulp produced by mills in this subcategory are viscose, nitration, or cellophane grades and are used principally for the manufacture of rayon and other products requiring the virtual absence of lignin.
8. HIGH ALPHA DISSOLVING SULFITE PULP means the production of highly bleached and purified pulp by a "full cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulfur dioxide.

The pulp produced by mills in this subcategory is principally acetate grade and the principal uses are for the manufacture of rayon and other products requiring the virtual absence of lignin.

9. SODA means the production by integrated pulp and paper mills of bleached pulp and paper by a "full cook" process utilizing a highly alkaline sodium hydroxide cooking liquor. The principal products made by mills in this subcategory are printing, writing, and business papers.

10. GROUNDWOOD: CHEMI-MECHANICAL means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing a chemical cooking liquor to partially cook the wood followed by mechanical defibration by refining at atmospheric pressure. The principal products made by mills in this subcategory are fine papers, newsprint, and molded fiber products.

11. GROUNDWOOD: THERMO-MECHANICAL means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, by a brief cook utilizing steam, with or without the addition of cooking chemicals such as sodium sulfite, followed by mechanical defibration by refiners which are under pressure. The principal products made by mills in this subcategory are fine papers, newsprint, coarse papers, and tissue products.

12. GROUNDWOOD: FINE PAPERS means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. The principal products made by mills in this subcategory are fine papers which include business, writing, and printing papers.

13. GROUNDWOOD: C.M.N. PAPERS means the production by integrated pulp and paper mills of pulp and paper, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. The principal products made by mills in this subcategory are papers of low filler content including coarse papers (C), molded fiber products (M), and newsprint (N).

14. DEINK means the production of pulp and paper usually brightened or bleached from recycled waste papers in which an alkaline treatment is used to remove contaminants such as ink and coating pigments. The principal products made by mills in this subcategory are printing, writing and business papers, tissue papers, and newsprint.

15. NON-INTEGRATED FINE PAPER means the manufacture of fine papers by non-integrated mills from wood pulp or deinked pulp prepared at another site. The principal papers made by mills in this subcategory are printing, writing, business, and technical papers.

16. NON-INTEGRATED TISSUE PAPER means the manufacture of tissue papers by non-integrated mills from wood pulp or deinked pulp prepared at another site. The principal products made by mills in this subcategory are facial and toilet papers, glassine, paper diapers, and paper towels.

17. NON-INTEGRATED TISSUE PAPERS (FROM WASTE PAPER) means the manufacture of tissue papers by non-integrated mills from recycled waste papers (fwp). The principal products made by mills in this subcategory are facial and toilet papers, glassine, paper diapers, and paper towels.

The effluent limitations and standards for the above subcategories are based upon on-site manufacture of all of the pulp (including deinking of waste paper) used to produce the final products (i.e., no supplementary fiber source such as purchased pulp or waste paper was included in the determination of the effluent limitations or standards). The exception to this is the Groundwood: OMN Papers and Groundwood: Fine Papers subcategories which were based upon groundwood mills manufacturing papers from pulp produced on-site and from purchased pulp used as supplementary fiber.⁽¹⁾ Of particular interest from the standpoint of PCBs and waste paper recycling are categories 14, 15, 16 and 17.

2.4 Papermaking Processes

2.4.1 Background

For most paper and paperboard products, the papermaking machine receives prepared paper stock containing about 199 pounds of water for every pound

of dry material, passes it through a series of operations to form it into a continuous web and to remove the excess water, presses the wet sheet to remove still more water and to make the sheet still more dense, dries it over heated driers and finally reels it up into large rolls. This change from stock containing almost ten tons of water per 100 pounds of dry matter to a sheet of paper which seldom contains over 5 pounds of water in 100 pounds of dry paper takes place in just a few minutes according to the speed of the machine. A schematic of the overall process is shown in Figure 2-1.

Although many mechanical variations and improvements have been made over the years, only two basic types of paper machines, the fourdrinier and the cylinder, are used today. Both were invented over a century ago. These machines differ significantly in the method of forming the fiber web.

The fiber stock is subjected to a series of refining and cleaning stages prior to its introduction to the paper machine. These stages are chosen to produce the desired fiber characteristics to meet the product's needs. The fiber stock is mechanically refined in heaters or continuous refiners to fray or "brush" the individual fibers. The frayed fibers will have a tendency to mat together and the degree of matting will produce the required strength in the final paper. In fine papers where a compact, tight mat is required the stock may also be pumped through a fordan which will cut the fibers to the required length with a limited amount of brushing.

2.4.2 Fourdrinier Paper Machine Process

In the fourdrinier, the refined stock is pumped to a headbox which controls the amount of stock flowing to the paper machine "wire" and thus maintains the paper at the desired consistency. The carefully diluted stock (~ 0.5% solids) is then spread evenly on the "wire" (a woven brass or bronze cloth, the mesh of which differs in type and size of opening according to the paper being made) to form the paper. Water drains through the wire, and is squeezed from below to assist in the drainage. The transfer of the sheet to presses is accomplished with a suction pick-up roll. The sheet leaves the "wet-end" of the machine at a consistency of 35 to 40% solids and is passed through heated, hollow iron or steel drum dryer rolls in the dry end. Because of its higher output speed and greater versatility the fourdrinier is more common than the cylinder.

Figure 2-1 gives a schematic process flow diagram for the fourdrinier paper machine. Of special interest is the recycling loop of both water and fiber from the fourdrinier section back to the rich white water tank, saveall and filtered white water tank. This stream is the major inplant carrier of fines-related PCBs, and is shown to be repeatedly passed through the fourdrinier to incorporate as much of the fiber and fines load as possible in the product paper.

2.4.3 Cylinder Paper Machine Process

In the cylinder machine, the headbox and wire found in the fourdrinier are replaced by a wire-covered cylinder mold which is partially immersed in the prepared stock.

The principle of the cylinder machine differs from that of the fourdrinier in several respects. Instead of the sheet being formed on an endless belt of woven wire through which the water drains, leaving the fibrous stock on its surface, the cylinder mold revolves while partially immersed in a vat of the dilute stock and the sheet is formed on the surface of the wire-covered mold. This is accomplished by maintaining the water level within the cylinder lower than that outside so that the water drains into the cylinder leaving the stock on its surface. The web of paper formed by the revolving cylinder is removed off the top of the cylinder by a felt. Usually a cylinder machine consists of several cylinder molds and vats supplied with stock entirely independently, and as the felt passes over each cylinder in turn it picks up the sheet from each, thus making a sheet of multiple layers. This makes it possible to form sheets with surface layers differing from those within the sheet, either in color, kind or fiber or both.

The same basic flow process is associated with cylinder machine as the fourdrinier shown in Figure 2-1; however, as mentioned above, the final product may be multi-layered, requiring a parallel stock flow through each cylinder machine.

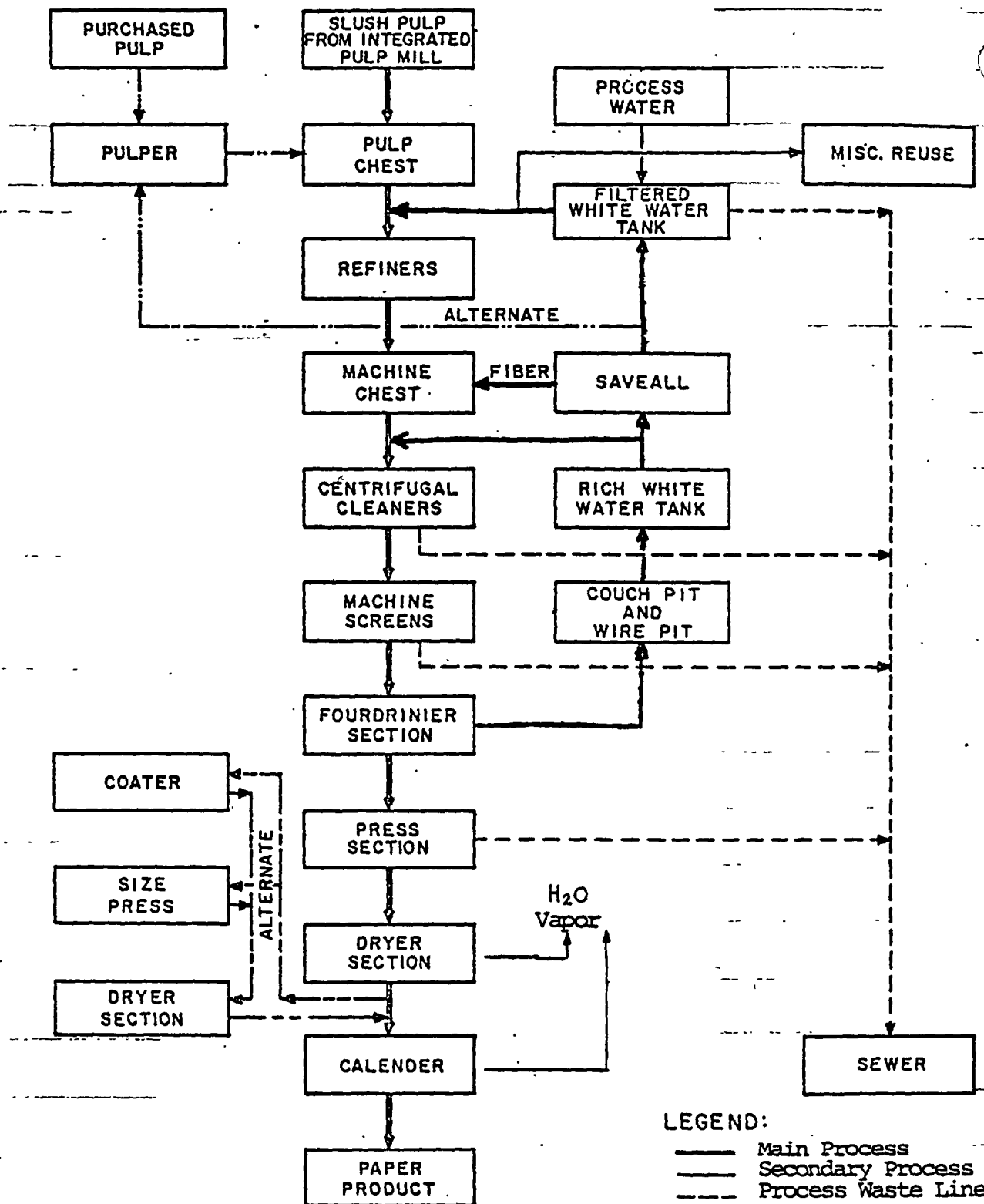


Figure 2-1

GENERALIZED SCHEMATIC OF PAPER PRODUCTION PROCESS

2.5 Paper Industry: Size and Distribution

2.5.1 Water Usage

Census Bureau data shows that Paper and Allied Products had a 1973 water intake of 2,415 billion gallons. Gross water usage was estimated to be 8,126 billion gallons. The ratio gross/intake shows how much water re-use is occurring. The historical trend is shown on Table 2-2.

Table 2-2
Water Usage in Paper and Allied Products Industries

<u>Year</u>	<u>Gross Water (billion gal)</u>	<u>Intake Water (billion gal)</u>	<u>Gross/Intake</u>
1973	8127	2415	3.36
1968	6522	2252	2.89
1964	5491	2064	2.66
1959	5046	1937	2.60
1954	4242	1786	2.38

Between 1954 and 1973 water intake increased by 35%. In the same period, total paper and paperboard production rose 106%. The trend to internal water recycling is well documented and continuing. A report by Rapson⁽²⁾ describes the processes to be used at the bleached kraft mill of Great Lakes Paper Co., Ltd. at Thunder Bay, Ontario. This mill will start up in late 1976 and will recycle virtually all of its water, emitting only low temperature heat in uncontaminated cooling water. Projections indicate this to be at a lower cost than use of external treatment. One major reason will be the conservation of heat in the counter current washing of the bleached pulp.

Allowing for a 5% water loss associated typically with product moisture, about 2.2 trillion gallons of water was discharged to U.S. waterways in 1973. Average runoff for the continental U.S. is given by Todd⁽³⁾ as 655 trillion gallons. A simple division indicates that the paper and allied product discharge is 0.33% of the total continental runoff. Since the discharge is not evenly distributed over the rivers, the water quality of even large streams can be strongly affected by the effluent loads from paper mills.

2.5.2 Production History

There is much potential for confusion in the utilization of data from the pulp and paper industry because over the years for which information has been retained, new products as well as new processes have appeared. As a result, the categorization of the output of the industry is constantly changing. While the categories are relatively stable over a short term period, they have changed noticeably during the long term. The general overall trend has been one of production increase, underlain with a use of recycled waste paper which has varied with world economic and political conditions. Table 2-3 shows the information on production and secondary fiber usage obtained from Bureau of Census, American Paper Institute and other sources for the 1957-1974 period.

According to the last column of Table 2-3, the rate of recycling has remained virtually constant at about 20% since 1968. Even with the emphasis on re-use and conservation of natural resources, little change can be seen. Lingle⁽⁴⁾ states that paper constitutes 31% by weight of municipal solid wastes going to disposal. Of that paper, 29% is corrugated containers, newspapers and printing papers are each 20%, and packaging and the other categories make up the balance. Slightly more than half of all paper wastes are from residences with the rest originating in commercial or institutional locations.

Source separation is a basic part of most collection systems focusing on recycling. Newspaper bundling in residential areas and compacted corrugated carton collection from commercial establishments are examples of such source separation schemes. This is required so that a paper mill utilizing recycled paper in its furnish (raw material) can be assured that the proper type of fiber is going into its process.

The type of catch-all waste which emanates from offices, government and commercial firms is termed "mixed waste". While it can be utilized by segments of the paper industry, there exists the chance in this waste stream for the carbonless copy paper which contains PCBs.

TABLE 2-3

Product Output and Recycle Rate

<u>Year</u>	<u>Paper (10⁶ tons)</u>	<u>Paperboard (10⁶ tons)</u>	<u>Construction Board (10⁶ tons)</u>	<u>Output Total (10⁶ tons)</u>	<u>Paper Stock Recycled (10⁶ tons)</u>	<u>% Production Recycled</u>
1957	13.6	14.1	3.0	30.7	8.5	27.7
1958	13.5	14.1	3.2	30.8	8.7	28.2
1959	15.0	15.5	3.5	34.0	9.4	27.6
1960	15.4	15.7	3.4	34.5	9.0	26.1
1961	15.7	16.4	3.4	35.6	9.0	25.2
1962	16.5	17.5	3.4	37.5	9.1	24.3
1963	17.3	18.2	3.7	39.2	9.6	24.5
1964	18.2	19.6	3.9	41.7	9.8	23.5
1965	19.2	20.8	4.1	44.1	10.2	23.1
1966	20.7	22.6	3.9	47.1	10.6	22.5
1967	20.9	22.1	3.9	46.9	9.9	21.1
1968	22.4	24.5	4.3	51.2	10.2	19.9
1969	23.6	26.1	4.5	54.2	10.9	20.1
1970	23.6	25.5	4.4	53.5	10.6	19.8
1971	23.8	26.1	5.1	55.1	11.0	20.0
1972	25.4	28.5	5.5	59.5	11.7	19.7
1973	26.5	29.7	5.7	61.8	12.2	19.7
1974	26.9	27.9	5.2	59.9	12.1	20.2

3.0 TRANSPORT OF PCBs IN THE PAPER INDUSTRY

3.1 PCB Sources to the Industry

3.1.1 Influent Waters

A representative value for PCBs concentration in the intake waters of paper mills was deemed necessary for several aspects of the work. This value, which was determined to be 0.1 ppb, was derived from several sources as shown below.

During the early months of 1976, EPA instructed its Regional Offices to conduct a sampling program aimed at identifying point sources of PCBs to the environment. This Regional Surveillance Program reported in excess of 2,400 data points. Of these, 106 could be unambiguously categorized as having come from a natural body of water. With the elimination of a few samples suspected of being contaminated, the average value of these "natural water" samples is 2.3 ppb. However, the choice of sampling sites was usually contiguous to a facility which was already a potential PCB emitter, so that this value is probably more representative of a high use, industrially developed stream rather than an environmental background. The intake PCB concentrations for paper mills might therefore be expected to be somewhat less than this 2 ppb average. Paper mills faced with suspended solids in their intake water will usually perform a clarification clean-up prior to use. Such treatment would be expected to remove up to 90 per cent of the PCBs from the water (retained on removed particulates).

Dennis⁽⁵⁾ obtained STORET data for PCBs in major U.S. drainage basins and showed a range of median values for each basin from ND (not detectable) to 0.3 ppb in his tabulation for 1974.

Data on intake water PCB concentrations from the Institute of Paper Chemistry for eight Wisconsin paper mills showed three mills reporting undetectable levels and the other five reporting an average of 0.2 ppb PCBs.

On the basis of the above considerations, the representative PCBs level of the water used in paper mills was taken to be 0.1 ppb.

3.1.2 Process Chemicals

Table 3-1 gives a typical listing of some of the major kinds of chemicals used in pulp and paper making. The amounts used on a per unit ton basis vary from trace quantities to 280 lbs. for some pulping liquor constituents.

Both Crown Zellerbach and Institute of Paper Chemistry researchers have tested process chemicals for PCBs. None have ever been detected except for one specialty chemical reported by IPC. A rough calculation shows that to produce a 2 ppm PCB concentration in a product which uses 8 lbs. of trisodium phosphate per ton of pulp (assuming a complete extraction of PCB by the fiber), 2 grams of PCB would have to come in with the detergent. Its concentration in the detergent would be 5500 ppm, easily detected. Even an increase of 0.1 ppm in the product from this source would require a concentration of 27.5 ppm in the phosphate. Present analytical capabilities allow monitoring at 1 ppm and below, so that PCB inputs from process chemicals would have been easily noticed.

3.1.3 Inks

The National Printing Ink Research Institute at Lehigh University was contacted for details on present and past usage of PCBs in printing inks. The major use reported was the NCR encapsulation procedure used in the carbonless copy paper. A small number of patents do exist for PCB use as part of some inks sensitive to ultraviolet light. However, they date from the very early seventies and had not gotten into widely marketed use by the time the PCB use in carbonless copy paper was stopped. To the best knowledge of NPIRI, none of these inks reached commercial production and no present day formulations utilize PCBs as a constituent.

Subsequent conversation with a representative of the Sun Chemical Co.* indicated that PCBs were used for several years prior to 1971 in "flexographic" inks used on flexible packaging. It was estimated that the production of such inks during 1970 was about 20 million pounds, of which about five per cent of the production would have contained PCBs at a two per cent by weight concentration. Thus, the estimated use of PCBs for this purpose, apparently the maximum, was 20,000 pounds in 1970. The historical trend for this application is not known, but based

*Personal Communication with Mr. William Rusterhaltz, Sun Chemical Co., October, 1976.

TABLE 3-1
REPRESENTATIVE CHEMICALS USED IN PULP & PAPERMAKING

<u>Name</u>	<u>Chemical Symbol</u>	<u>Amount lbs/Ton Pulp</u>	<u>Uses/Remarks</u>
Ammonia	NH_3	90-120	Sulfite pulping
Nitric Acid	HNO_3		Nitric acid pulping
Sodium hexametaphosphate	$\text{Na}_{16}\text{P}_{14}\text{O}_{11}$	2-4	Pitch dispersant for sulfite pulp
Sodium tripolyphosphate	$\text{Na}_3\text{P}_3\text{O}_{10}$	10	Sequesterant for brightness
Trisodium phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	4-8	Deinking detergent
Sodium Sulfate	Na_2SO_4		"Salt cake", Kraft pulping make-up
Sodium pentachlorophenate	$\text{C}_6\text{Cl}_5\text{ONa}$		Slime control
Sodium Sulfite, anhydrous	Na_2SO_3	140-280	Cooking liquor for neutral sulfite semi-chemical pulping
Sodium Acid Sulfite	NaHSO_3		Buffer, removes residual chlorine from bleached pulp
Sodium Carbonate	Na_2CO_3		Deinking, "soda ash"
Surfactants	Dodecylphenol of ethylene	10-13	Deresination of pulp
	Oxide bases	4-8	Deinking and defibrization of waste paper
Sulfur Dioxide	SO_2		Bleaching
Sulfuric Acid	H_2SO_4		pH control, reducing agent for NaClO_3
Aluminum chloride	AlCl_3		Alum replacement
Sodium hydroxide	NaOH		Bleaching, deinking, "caustic soda"
TCC	3,4,4 trichlorocarbonyl chloride		Bacteriostat (microbiological control) substantive to cellulose
Hydrochloric acid	HCl		pH adjust, cleaning agent
Orthodichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$		Cleaning solvent for felts
Phosphoric Acid	H_3PO_4		Brightener, precipitates Ca. a phosphate
Miscellaneous			A large number of special purpose additives; sweeteners like saccharin, odorants like ethyl vanillin, and so on.

on a five-year period of usage and linear growth during that period, it is estimated that the total usage of PCBs in such inks was about 50,000 lb.

The above figure is roughly 0.1 per cent of total PCBs usage in carbonless copy paper. In addition, flexible packaging materials typically were plastic or contained plastic adhesives which render them unattractive for recycling. Thus, it appears unlikely that the PCBs usage in flexographic printing inks has contributed significantly to PCBs inputs to the paper industry.

3.1.4 Recycled Waste Paper

As was indicated in Section 1.0, the major source of PCBs entry into the paper industry appears to have resulted from the use of Aroclor 1242 in carbonless copy paper during 1957-71 and subsequent recycling of a fraction of this product. To some extent, PCBs contamination has spread from this source throughout paper products because of the affinity of paper for PCBs. A summary of available data on PCBs levels in various types of paper products, by year, is presented on Table 3-2. The recycling of these products tends to perpetuate the contamination.

3.1.5 Other Potential Uses or Sources of PCBs in Paper Mills

Although paper mills utilize askarel-filled (PCB) transformers and capacitors, and may have utilized PCB-filled hydraulic or heat transfer systems, PCB-containing lubricants, paints, etc., it is considered unlikely that such activities would be causing release of significant quantities of PCBs to either effluent streams or product streams.

Similarly, it is also considered highly unlikely that PCBs are produced in the practice of wastewater chlorination in the paper industry. Biphenyl has not been identified as a waste stream constituent from this industry, although very small amounts could conceivably enter via recycling of packing materials (typically for fruit) which have been treated with biphenyl as a fungicide.

3.2 PCB Content of In-Plant Streams and Reservoirs

Data on PCB levels of in-plant process streams are almost completely nonexistent for three apparent reasons. First, at the observed low concentrations, PCBs have no effect on product quality, so that internal monitoring is not required.

TABLE 3-2

PCB CONTENT OF PAPER AND PAPERBOARD

		No. of Samples	PCB Content (ppm)	Reference
1968	Virgin pulp	2	0.29	6
Prior to 1970	Recycled ⁽¹⁾ wastepaper input	13	3.2	6
1971	Recycled ⁽¹⁾ wastepaper input (1970-1972)	24	1.1	6
1972	Recycled paperboard	200	15.3	7
	Virgin pulp	2	0.16	6
1973	Paperboard	100	0-20	8
1973	Virgin newsprint	3	<.5-1.0	9
	Recycled newsprint	3	<.5-1.38	9
	Virgin bond paper	7	<.5-8.5	9
	Recycled bond paper	2	113.5-290	9
	Bleached kraft pulp	4	<.5-1.33	9
	Bleached kraft liner board	1	<.5	9
	Publication paper	3	<.5	9
1974	Recycled paperboard	115	1.45-2.97	7
	Recycled ⁽¹⁾ wastepaper input	5	0.37	6
	Virgin pulp	2	0.127	
1975	Paperboard	4	0.3-1.2	10
	Virgin pulp	6	0.072	11
1976	Paperboard	-	0.430	11
	Cereal liner	-	0.8	6
	Corrugated board	-	0.2	11
	Waxed paper	-	0.5	11
	Spec. twist	-	0.2	11
	Lamin. grade	-	0.3	11
	Bookstock	-	1.6	11
	Recycled ⁽¹⁾ wastepaper input	138	0.15	6

⁽¹⁾ Discounting known samples of NCR carbonless copy paper.

Second, most plants, especially the older ones, are not planned with specific capability for sampling in-plant flows, so any sampling done is more by opportunity than by design. Thirdly, commercial PCB analyses cost from \$60 to \$100 per sample, and a sampling program without a clear goal of compliance with regulations or product improvement is generally considered a poor investment. A PCB analytical system would require capital costs in the range of \$15,000 to \$20,000 and annual expenditures for trained personnel, lab space, and operation of up to \$50,000.

3.2.1 PCBs in Deinking and Pulping Process Water

The deinking process water is typically not a recycled stream, although in many cases it represents a significant fraction of the total water usage for a recycling mill. Deinking procedures and conditions depend on the product qualities desired (white or natural or color, etc.). Although some of the PCBs associated with recycled paper will probably be stripped from the fibers during deinking, this should represent only a minor fraction of the total PCB load of the reclaimed material.

During the pulping process the cellulose fibers are separated, and this process should also release the PCBs or PCB-containing microballoons held within the mat. PCBs already released from microballoons would then be able to distribute themselves between the fibers and the water. Since evaporation and other losses of PCBs during pulping should be small, the above appears to be the situation when the slush pulp enters the paper mill.

3.2.2 Distribution of PCBs in the Papermaking Process

In the papermaking process (see Figure 2-1), most of the PCBs entering with the pulp exit with the product. These would include most of the PCBs in intact microballoons and most of the PCBs associated with fibers. In the drying and calendaring sections, the vaporization of excess water would be expected to codistill free (not encapsulated) PCBs at or near the surface. This is the major opportunity for vaporization loss in the process.

In a typical plant, much of the water in the papermaking process (white water) is recycled as shown in Figure 3-1. White water from the fourdrinier or cylindrical machines contains dissolved and suspended PCBs. The fibers present

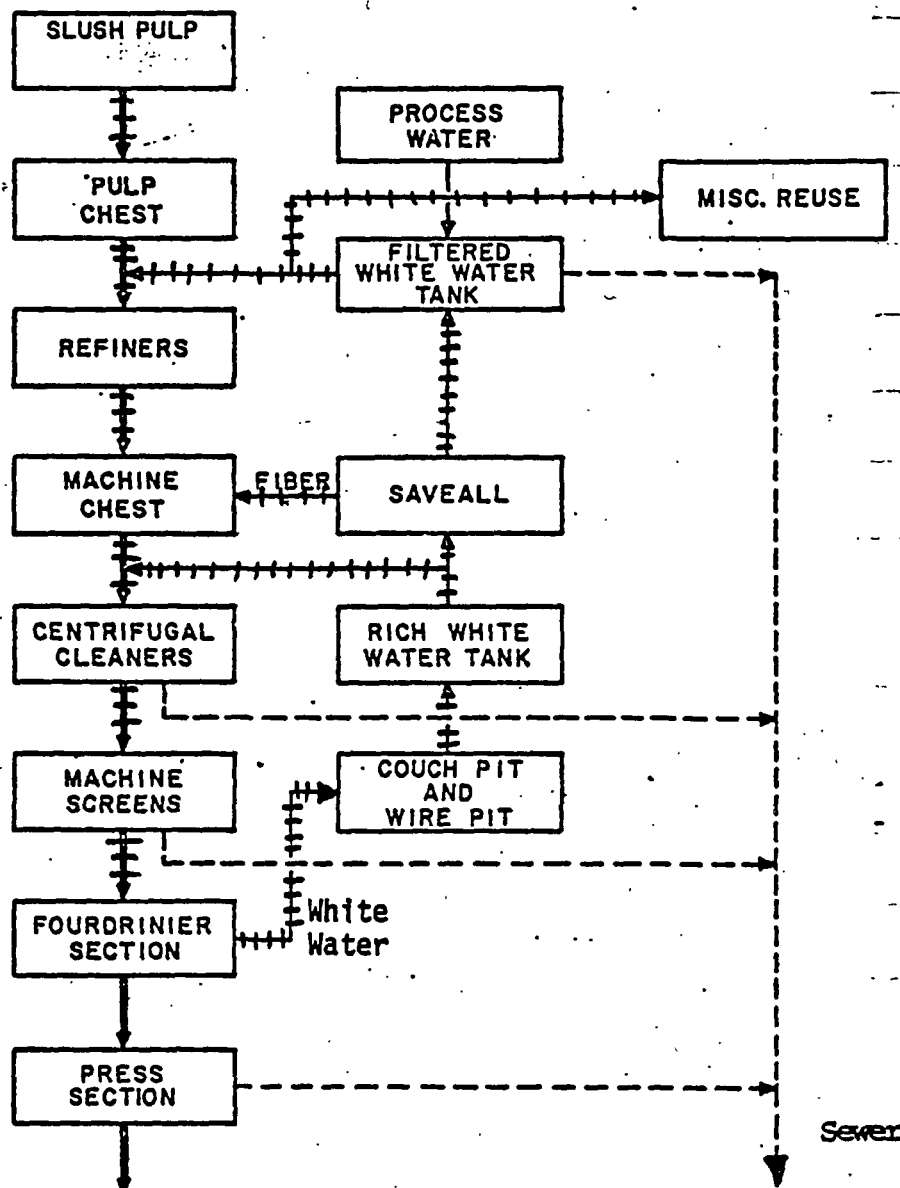


Figure 3-1
Major Fiber and Water Routes in Paper Production

are relatively small, with high surface area per unit weight, so that the ratio of PCBs to solids by weight may be as large as or greater than the PCBs content of the product. Much of the PCBs in suspended form is added back to the main process with the short fibers, in order to conserve fiber. The liquid phase from the "save-all", a separator unit, is filtered to further remove fiber (which goes back into the process) and the filtrate is discharged. This clarified save-all yield can be one of the major components of the discharge from the plant.

If we assume a 1 ppm PCB concentration (typical of product PCB levels using recycled pulp) in the fiber portion of the clarified save-all yield (at 120 mg/l solids), the PCB concentration of that flow is 0.12 ppb which is effectively the same as the intake value selected as representative, and near the lower working limit of present analytical techniques. About 95 per cent of the PCBs entering the save-all appear to be directly recycled back into the paper on the PCBs first pass through the white water system. Thus, it appears that most of the PCBs (and the solids) in the effluents arise from unit processes other than the save-all.

Since it appears that most of the PCBs in paper mill effluents are associated with the fiber solids (either encapsulated or adsorbed PCBs), the major route of PCBs entry into wastewaters must then be via solids entry. On Figure 3-1, this occurs primarily in the aqueous discharges from the centrifugal cleaners, machine screens, and press section. Fiber loss at these points is sufficient to cause solids levels up to several grams per liter in the raw wastewater.

3.2.3 Fate of PCB-Containing Microspheres

The hardened gelatin-gum arabic walls of the ink-carrying microballoons used in the NCR carbonless copy paper are considered essentially stable under conditions typically encountered in the use of secondary fiber. Thus, most of the microballoons should proceed through the process intact. Most would be expected to be incorporated into the product, because of the manner in which fiber is collected in to product (essentially a filtration process).

Based on the above, the PCBs content of the plant effluent should consist of those microspheres not retained in the product and a fraction of that released by breakage (through usage of the paper, during collection and transport of wastes, and in the recycling and papermaking processes). The remainder of that released by breakage could remain on the product, be vaporized, or removed from the stream in various other ways.

This line of reasoning leads to the conclusion that most of the PCBs in paper products and wastepaper is still encapsulated. Discussions with paper industry representatives have supported this view, especially discussions on the comparison of analytical results between procedures in which the microballoon walls have and have not been definitely destroyed. PCB levels resulting from destruction of the microsphere walls with alcoholic potassium hydroxide solution are much higher than those obtained using conventional extraction procedures. However, this could be grossly misleading since the same treatment is necessary to separate the individual fibers to release for analysis PCBs (in whatever state) trapped within the mat.

The actual proportion in paper products and effluents of PCBs in intact microballoons is not known and could be ascertained only with difficulty. One of the items of future work proposed by the Institute of Paper Chemistry in a recent report⁽¹²⁾ is to determine the amount and effect of PCBs present in products and effluents within intact microballoons.

3.3 PCB Losses from the Pulp and Paper Industry

3.3.1 Wastewater

The PCBs content of microballoons in plant effluents can be removed by solids removal; similarly, PCBs sorbed onto suspended solids in the effluent can likewise be removed. Solubilized PCBs, either in true solution or present in or on very small particulates, will be very difficult to remove from effluents.

The partition coefficient for PCBs between cellulose and water is not expected to be anywhere near as large as those between lipids or carbon (for example) and water, based on the relatively slight accumulation in woody plants

and scanty general information available on this subject. Unpublished data obtained from the Institute of Paper Chemistry concerning a series of experiments in which one per cent fiber slurries in water were doped with PCBs (up to 100 ppb), shaken and allowed to settle, and then filtered and analyzed, indicated partition coefficients ranging from 800 to 1700. These values are not sufficiently high to allow removal of dissolved PCBs with suspended solids in mill wastewaters as described below.

At a partition coefficient for PCBs between cellulose and water of 500, and a suspended solids content of two gm/liter, about one-half of the "free" PCBs would be expected to be adsorbed onto the fiber. However, recent industry experience has indicated that removal of over 90 percent of the suspended solids from the wastewaters will also remove over 90 percent of the PCBs, with resulting PCB concentrations in the range of 0.1 ppb to several ppb, well below the reported solubility level of Aroclor 1242. In the absence of other information, this appears to indicate that relatively little of the PCBs in the wastewater is present as dissolved PCBs.

Three alternative explanations for the above appear to be possible:

- (1) The partition coefficient between water and the solids present is very much greater than a few hundred;
- (2) Most of the PCBs present are encapsulated in microballoons and are thus removed in this form along with the other solids; or
- (3) Organic solids added to or present in wastewater treatment systems serve to separate the PCBs from the water.

Alternatives (2) and (3), or a combination of these, appear to be more likely than alternative (1). In all paper mill wastewater treatment systems of which we are aware, polymeric flocculation aids are added in primary treatment and/or the water is subjected to activated sludge secondary treatment. It is well-known that biological sludges exhibit a strong affinity for PCBs and, although the sorptive activity of the polymeric agents for PCB relative to water (and cellulose) is not known, it may be surmised that these agents are better scavengers of PCBs than cellulose. However, alternative (2) (most PCBs still encapsulated) remains a strong possibility until proven otherwise.

The PCB levels in raw wastes from recycling plants vary widely but are typically in the range of 10 to 100 ppb. With current waste treatment practices, this is reduced to a typical range of less than 0.5 ppb to several ppb, with occasional excursions. As a consequence of the recent experience showing PCB removal concomitant with suspended solids removal, compliance with BPCICA (1977) and BATEA (1983) should result in continuation of the downward trend in effluent PCB levels.

3.3.2 Vaporization Losses

3.3.2.1 Losses During Papermaking

Available information indicates that there may be measurable losses of PCB during the removal of moisture from the paper in the dryer section of the machine. This conclusion was reached on the basis of mass balance studies done on a number of cooperating Wisconsin mills.

We are dealing here with a PCB concentration in a typical paper of only 1 gram per ton. Since the qualitative assessment of the vaporization loss was that it was a few percent of the PCBs present, the loss will not pose a health hazard, nor will it have a significant effect on the conclusions reached in the model of the industry.

3.3.2.2 Losses from Effluent Treatment Ponds

A significant amount of the treatment of papermill effluent occurs in systems open to the atmosphere. Such choices as aerated stabilization basins, ditch aeration, and rotating biological surfaces are designed to provide a greater supply of atmospheric oxygen to the effluent for the purposes of lowering BOD. At the same time an opportunity arises for PCBs to exchange across the solid-liquid and liquid-gas interfaces. No definitive data on these processes for PCB loss are available, but there may be the possibility of exchange mediated by the partitioning of the PCBs in the complex systems.

One expects some exchange based on previously published descriptions of apparent losses from natural water systems such as Lake Michigan⁽¹³⁾, as well as demonstrated losses from 1 per cent pulp fiber/distilled water slurries

in experiments carried out at the Institute of Paper Chemistry. The latter case showed up to 30 per cent losses from solutions spiked to the 100 ppb concentration.

Quantitative assessment of the evaporative losses from actual treatment facilities will require application of field sampling techniques for airborne PCBs which are still in the development stage.

3.3.3 Incineration Losses

Destruction of PCBs by high temperature incineration is generally regarded as requiring a 2 to 3 second exposure to 2,000°F for "complete" combustion. Shorter contact times or lower temperatures will not allow complete elimination of these stable compounds. Specially designed incinerators have been operated by Monsanto and other firms for the proper decimation of PCB-containing liquid wastes, but typical municipal and industrial incinerators will not destroy PCBs completely.

3.3.3.1 Bark Burning

In those mills which practice barking, the bark is often utilized as a hog fuel in mills which generate sufficient bark to use it to fire a boiler for steam generation. Smaller producers of bark may simply incinerate it along with unsalvageable fiber from other parts of the operation. Like the virgin wood, bark has a PCB content which is essentially nil and results in an extremely tiny emission to the atmosphere under these conditions.

3.3.3.2 Sludge, Spent Liquor and Carbon Burning

On an industry-wide basis there has been a drastic decrease in incineration of these materials. The price of fuel necessary to mix with them has risen to the point where alternative disposal schemes cost less.

Sludge is dewatered and generally landfilled. Its PCB content usually ranges from 4 to 25 ppm, the same range exhibited for municipal treatment plants.⁽¹⁴⁾ As such, it should be subject to the same careful handling as other PCB wastes.

Spent liquor of all types is being internally recycled and refined to reduce the amount of make-up chemical required in the pulping stages. More and more opportunities are being discovered for converting spent liquors into

salable by-products or for conversion to other uses inside the plant. These reasons have led to a great overall reduction of liquor burning throughout the industry.

Charcoal burning has been used in a few instances for the production of carbon. But the extent is not great and one would expect volatilization of any PCBs to have taken place prior to such an activity. As in bark burning, actual measurements of such potential losses are not available.

3.3.4 Solid Process Waste Losses

The industry exhibits an average process loss of 2 to 5 per cent. That is, of the pulp entering the paper machine, 2 to 5 per cent of the fiber by weight does not get incorporated into the product paper. This amounts to 40 to 100 pounds of solids per ton of product that will be incorporated into the sludge. As mentioned in the previous section, the few data for paper mill sludge PCB content shows it to be in the same range exhibited by municipal treatment plant sludges. These considerations predict that an average mill with 100 ton daily production might landfill between 2 and 120 grams of PCBs per day (0.004 - 0.26 lbs.)

The effective mobility of PCBs in the landfill situation is not well described. The EPA Regional Surveillance Program generated 75 samples described as leachates. These were all samples where ground water was determined to have had the opportunity to percolate prior to sampling.

Eliminating three samples known to be directly associated with highly contaminated industrial sites, the average value for the 72 remaining samples is 2.8 ppb. It is only 2.8 times the 1 ppb detection limit specified in the EPA 40 CFR PT.136 standard analytical method.

Assuming that landfills are about 40 to 50 per cent paper, neither the paper or the sludge would appear to be mobilizing large quantities of PCBs. In fact, the leachate PCB concentration is indistinguishable from that of industrial intake waters reported by the Regional Surveillance Program and described in Section 3.1. The binding of the PCBs to the fiber may be similar in stability and strength to their association with soil or sediment particles. PCB mobility in sediments is reported to be very low. (15,16,17) This is thought to be due to the availability of organic material with which PCBs preferentially associate.

3.3.5 PCB Concentration in Finished Product

Product concentrations are referred to elsewhere. In general, PCB levels of current products made with recycled fiber range up to one to two parts per million. This material appears to be almost entirely due to use of Aroclor 1242 in NCR carbonless copy paper prior to the spring of 1971. Levels in products appear to be consistently decreasing since the 1971-72 time frame.

3.4 Monitoring Technology

The study of PCBs within the pulp and paper industry is naturally based on the data generated by the analytical procedure. At the present time, just as in the analysis of natural waters for PCBs, there is no standard method for the analyses of pulps or effluents which take into account the peculiarities of the matrices involved. For example, in the analysis of pulp or paper, it is absolutely essential to remove the PCBs from the fiber quantitatively so that eventual extraction into an organic solvent such as hexane may be accomplished. Removal procedures such as treatment with alcoholic potassium hydroxide have been used. Application of surfactants such as Triton X-100 is also practical. Having removed the PCBs from the fiber, it is then necessary to make sure that both forms, the free PCB and the encapsulated PCB from NCR carbonless copy paper, are extracted into the solvent.

There exists a definite problem with storage of samples prior to extraction and analysis. Apparently, the organic activity of the bacterial population immobilizes PCBs in slimes deposited on container walls and fiber. An attempt to control such losses has been to add formaldehyde to the samples, killing all biotic activity. This has proven successful in lake and stream waters.⁽¹⁸⁾

EPA researchers recommend that the extraction step be performed on a vortex mixer in the original container. This is to give the solvent the maximum opportunity to react with any of the analyte bound to the container walls. It also will assist in reducing volatilization losses already shown to be potentially large by the Institute of Paper Chemistry.⁽¹²⁾ Similarly, it has been recommended that all transfers of material during the pre-analysis manipulations be kept to an absolute minimum.

Limited intercalibrations have shown the drastic effects on precision and accuracy which the small differences in sample handling and storage can have. One IPC study showed 3 laboratories reporting 21.5 ppb, 102 ppb and 180 ppb on a split effluent sample. But while other samples showed as large percentage differences, there was no regularity in the laboratories reporting high or low on a given sample. IPC and others are working in the vicinity of a 0.1 ppb detection limit in effluent samples. Most of these intercalibrations took place at concentrations far above the detection limits so noise in the analysis is small compared to irregularities introduced by storage and handling.

Quantitation of the chromatogram is a difficult process for the complex, multi-peaked plots given by PCBs. Paper mill effluents often show interfering peaks caused by non-PCB materials. Recourse to mass spectroscopy analysis is sometimes necessary to separate these interferents. Some removal is accomplished by sample oxidation with chromium trioxide, but many peaks can remain and a qualitative assessment of the chromatogram by a trained person must be employed. The possibility of mis-identification is real, but the alternative use of the GC-mass spectrometer is often too expensive to be considered for routine use.

The continuing decline in PCB concentrations in effluent, sludge and product will require a continuing improvement in detection limits and sample treatment techniques.

A detailed treatment of analytical techniques for PCBs in paper products and paper mill effluents is presented in Reference (12).

4.0 COST DEVELOPMENT OF PCB REMOVAL FROM PAPER RECYCLING MILL EFFLUENT STREAMS

4.1 Background

The major apparent cause of PCBs in this industry is the use, until 1972, of Aroclor 1242 in carbonless copy paper. A significant portion of this paper has gone through at least one recycle resulting in the PCB contamination of the effluents emanating from these facilities.

Three major types of paper recycling mills currently exist in the U.S. They are:

- (1) Mills producing paper products with deinking process;
- (2) Mills producing paperboard from wastepaper; and
- (3) Non-integrated mills producing tissue paper from wastepaper without deinking.

A number of mills in the paper recycling industry are so-called complex mills, i.e., mills which produce multiple paper grades. The basis used for classifying complex mills is the product and process which account for the largest daily production capacity. Table 4-1 summarizes the distribution and the production of the paper recycling industry in the U.S.

The general process used in the paper recycling industry is pulping and deinking (only for deink mills), pulp washing, bleaching (not for paperboard mills), screening and cleaning, and papermaking. PCBs can be released from the recycled paper in any or all of the above process steps. The water usage of a deinking plant is large and can amount to 65 percent of the total usage of the entire mill. Water used in pulp washing is generally done in a counterflow system which allows maximum potential for water reuse. Some characteristics of the effluent streams are shown in Table 4-2. Data on the PCBs level in the effluent streams for this industry are discussed in Section 3.3.

Technologies for the removal of PCBs from industrial wastewater were evaluated and described in a previous report.⁽¹⁹⁾ Carbon adsorption in conjunction with pretreatment (equalization and multimedia

TABLE 4-1

SUMMARY OF DISTRIBUTION AND PRODUCTION
OF THE PAPER RECYCLING INDUSTRY¹

<u>Category</u>	<u>No. of Plants in U.S.</u>	<u>Annual U.S. Production</u> kkg (ton)/yr	<u>Annual Average Plant Production</u> kkg (ton)/yr.
1. Deink	17	1,000,000 (1,100,000)	58,800 (64,600)
2. Paperboard from wastepaper	165	6,900,000 (7,600,000)	41,800 (45,900)
3. Non-integrated tissue papers from wastepaper without deinking	Not Available ³	Not Available ³	11,680 (12,800) ²

¹Source - EPA reports 440/1-76/047-a and 440/1-74/025-a²Average of 4 plants³There are a total of 72 non-integrated tissue mills in the U.S. with total capacity of 6,300 kkg/day (6,900 tons/day). No information was obtained as to how many plants actually recycle wastepaper

TABLE 4-2

EFFLUENT CHARACTERISTICS OF THE
PAPER RECYCLING PLANTS¹

<u>Category</u>	<u>Effluent Flow Rate</u>	<u>[BOD], mg/l</u>	<u>[TSS], mg/l</u>
	1,000 l/kg of product (1,000 gal/ton)		
1. Deink	range, 55.5 (13.3) - 93.0 (22.3)	40 - 197	45 - 141
	average, 74.0 (17.8)	92	97
2. Paperboard from wastepaper	range, 5.0 (1.2) - 68.4 (16.4)	9 - 82	40 - 83
	average, 30.0 (7.2)	46	164
3. Non-integrated tissue paper from wastepaper	range, 27.9 (6.7) - 79.2 (19.2)	146 - 411	Not available
	average, 53.6	279	Not available

¹Source - EPA reports 440/1-76/047-a and 440/1-74/025-a.

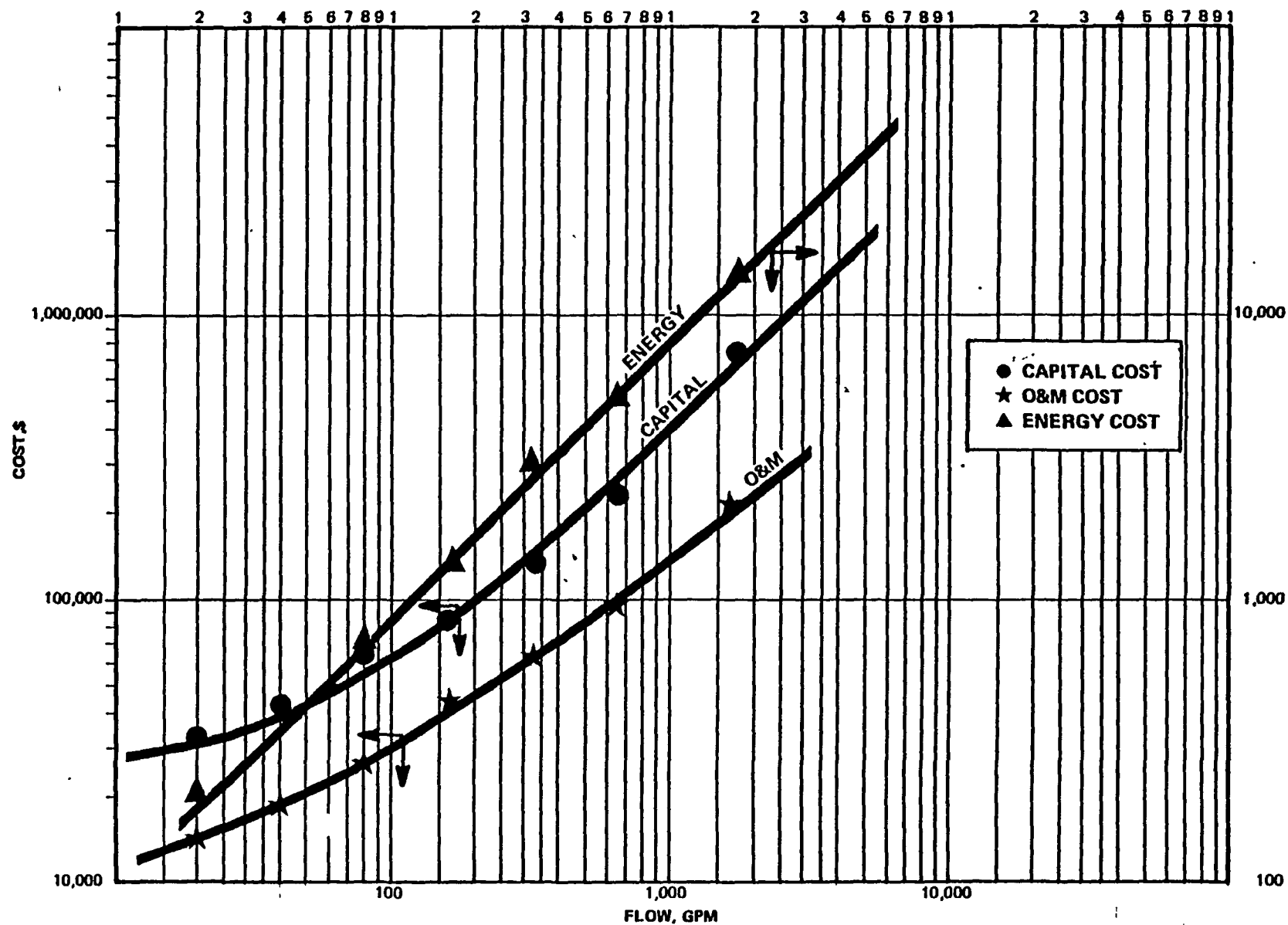


Figure 4-2. CARBON ABSORPTION WASTEWATER TREATMENT SYSTEM COSTS

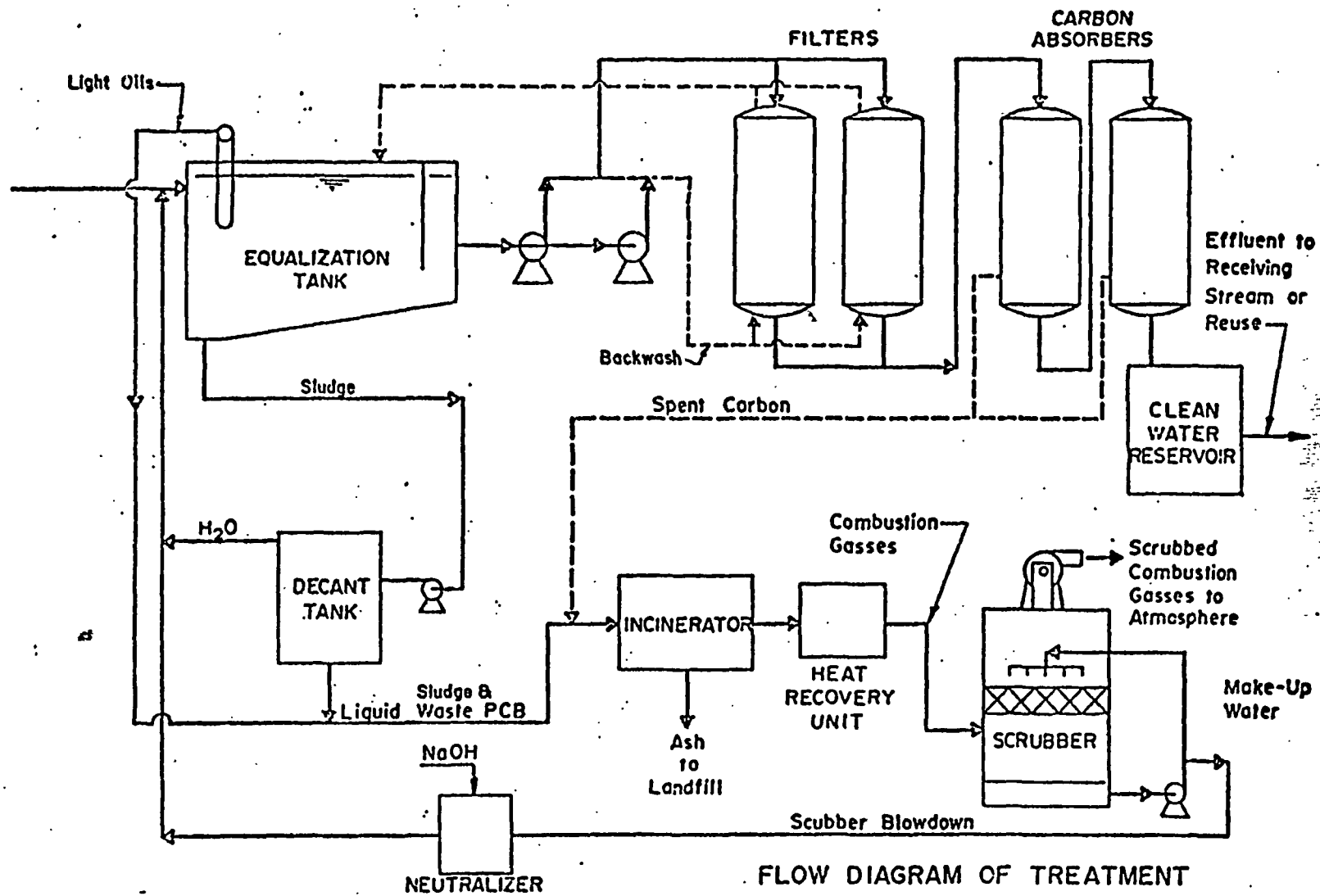


Figure 4-3.

FLOW DIAGRAM OF TREATMENT
SYSTEM FOR REMOVAL OF PCB
FROM WASTE WATER

tion basin at an unknown concentration and leave it at 200 ppb, and that filtration will reduce the PCBs level to 50 ppb. Subsequent terminal treatment systems, i.e., carbon adsorption will reduce this PCBs concentration to 1 ppb or less. Plants which already have treatment for suspended solids and discharge less than 50 ppb of PCBs in their effluent streams may install the carbon absorption system only.

4.3 Cost References and Rationale

The basic assumptions and rationale employed in developing the wastewater treatment costs in the paper recycling industry for PCB removal can be summarized as follows:

- (1) Costs are developed for "representative plants" rather than any actual plant. "Representative plants" are defined to have a size, age, and wastewater flow agreed upon by a substantial portion of the manufacturers in this category. In the absence of such information, the arithmetic average of production size and wastewater flow for all plants is used. It should be noted that the unit costs to treat wastes at any given plant may be considerably higher or lower than the representative plant because of individual circumstances. Extrapolation of these costs to the entire industry would very likely be unrealistic.
- (2) The costs for the end-of-pipe treatment for PCBs are assumed to be essentially proportional to the volumetric flow rate of the wastewater. The treatment costs developed in the previous report⁽¹⁹⁾ for PCB removal are reassembled and presented in Figures 4-1 and 4-2.

- (3) Very limited amounts of information are available from this industry concerning the PCB concentration in the effluent and the kinds of treatment presently employed. Therefore, the estimated total annual cost for PCB wastewater treatment of a representative plant is based on the "worst case" conditions. It was assumed that "representative plants" employed no terminal treatment for PCBs removal and practiced no segregation of wastewaters containing PCBs from other in-process use waters.
- (4) Costs are developed separately for the pretreatment (equalization and multimedia filtration) and the carbon adsorption treatment of PCBs.
- (5) The capital cost is based on 8 percent interest over a period of ten years. If the supply of waste paper with substantial PCB content stops before the ten-year period is up, the capital recovery cost will increase substantially.

4.4 Cost Development

Three major categories are identified within the paper-recycling industry (see Section 4.1). The costs of wastewater treatment are developed for each individual category. Costs for pretreatment and carbon adsorption for each category are shown in Tables 4-3 through 4-5. The capital costs, operating and maintenance costs (excluding power), and power costs are taken directly from Figures 4-1 and 4-2 at given wastewater flow rates. Throughout the analysis represented by Tables 4-3 through 4-5, annual capital recovery costs were calculated based upon a ten-year lifetime and an 8 percent interest rate, consistent with the earlier reference.⁽¹⁹⁾ The capital recovery factor was thus estimated to be 0.15. All cost estimates contained in this report are based on 1976 dollars.

TABLE 4-3

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Deink Paper Manufacture
 PLANT SIZE: 58,800 Metric tons of product/year
 FLOW: 8,210 l/min (2,170 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		<u>Total Treatment System</u>
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	
Invested Capital Costs:			
Total	4,600,000	860,000 *	5,460,000
Annual Capital Recovery	690,000	129,000	819,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	78,000	250,000	328,000
Annual Energy and Power	58,000	17,000	75,000
Total Annual Costs	826,000	396,000	1,222,000
Cost/Metric Ton of Product	\$14.11	\$6.78	\$20.89

*Actual costing on a specific mill showed that this amount could be raised by 275% in an individual case.

TABLE 4-4

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Paperboard from Wastepaper
 PLANT SIZE: 41,800 Metric tons of product/year
 FLOW: 2400 l/min (630 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		<u>Total Treatment System</u>
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	
Invested Capital Costs:			
Total	1,500,000	260,000	1,760,000
Annual Capital Recovery	225,000	39,000	264,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	32,000	100,000	132,000
Annual Energy and Power	16,000	5,000	21,000
Total Annual Costs	273,000	144,000	417,000
Cost/Metric Ton of Product	\$6.50	\$3.43	\$9.93

TABLE 4-5

COST ANALYSIS FOR A REPRESENTATIVE PLANT

CATEGORY: Non-integrated Tissue Paper from Wastepaper

PLANT SIZE: 11,680 Metric tons of product/year

FLOW: 1,200 l/min (310 GPM)

<u>Type of Cost</u>	<u>Treatment Costs, Dollars</u>		
	<u>Pretreatment</u>	<u>Terminal Treatment via Carbon Adsorption</u>	<u>Total Treatment System</u>
Invested Capital Costs:			
Total	860,000	140,000	1,000,000
Annual Capital Recovery	129,000	21,000	150,000
Operating and Maintenance Costs:			
Annual O&M (excluding power and energy)	19,000	60,000	79,000
Annual Energy and Power	8,000	2,600	10,600
Total Annual Costs	156,000	83,600	239,600
Cost/Metric Ton of Product	\$13.36	\$7.16	\$20.52

A summary of cost estimates for PCB removal at different input PCB levels is given in Table 4-6. A summary of total capital investment cost information for PCBs from paper recycling mill effluent is given in Table 4-7. Based upon the information contained in this table, this industry, as a whole, would have to invest up to an estimated maximum of \$366,700,000 to achieve a PCB limitation of 1 ppb in their wastewaters. There is also an anticipated \$94,120,000 of annual treatment cost for the removal of PCBs from this industry. Table 4-8 is a summary of the treatment cost of PCB removal. The estimated annual treatment costs correspond to a three to five percent increase in the selling prices of products from this industry.

Depending on the amount of pretreatment required to decrease the suspended solids to a point where fouling of the charcoal beds could be avoided, costs could escalate severely. Such would be the case for effluents from deinking operations where fines loading can be heavy and particle sizes quite small.

TABLE 4-6

SUMMARY OF ESTIMATED CARBON ADSORPTION
TREATMENT COST AT DIFFERENT INPUT PCB LEVELS

<u>[PCB] Input</u> <u>(ppb)</u>	<u>Estimated Annual Carbon Adsorption Costs</u> <u>\$/kg of PCB Removed (\$/lb)</u>		
	<u>Deink</u>	<u>Paperboard</u>	<u>Tissue</u>
50	1,870 (850)	2,330 (1,060)	2,730 (1,240)
40	2,350 (1,070)	2,930 (1,330)	3,430 (1,560)
30	3,160 (1,430)	3,940 (1,800)	4,610 (2,090)
20	4,820 (2,190)	6,020 (2,730)	7,030 (3,190)
10	10,200 (4,620)	12,700 (5,770)	14,800 (6,740)
5	22,900 (10,400)	28,600 (13,000)	33,400 (15,200)

TABLE 4-7

SUMMARY OF CAPITAL INVESTMENT OF PCB
REMOVAL FROM PAPER RECYCLING INDUSTRY

	Total Capital Investment in Industry, ¹ Dollars		
	<u>Pretreatment</u>	<u>Carbon Adsorption</u>	<u>Total</u>
Deink	78,200,000	14,600,000	92,800,000
Paperboard from wastepaper	247,500,000	6,440,000	253,900,000
Non-integrated tissue paper from wastepaper without deink	17,200,000	2,800,000	20,000,000
Total	342,900,000	23,800,000	366,700,000

¹Assume all plants in each category have production rates similar to the representative plants.

TABLE 4-8
SUMMARY OF COSTS OF PCBs REMOVAL
FROM PAPER RECYCLING INDUSTRY

<u>Category</u>	<u>Total Annual Costs (\$/kgg of product)</u>	<u>Present Selling Price (\$/kgg of product)</u>	<u>Annual Cost as percent of Selling Price</u>	<u>Total⁴ Annual Cost in Industry (\$/yr)</u>
Deink	20.89	440 - 550 ¹	3.8 - 4.7	20,900,000
Paperboard from wastepaper	9.93	220 - 330 ²	3.0 - 4.5	68,500,000
Non-integrated tissue paper from wastepaper without deinking	20.52	Not available ³	Not available ³	4,720,000 ⁵
Total				94,120,000

¹Personal communication between C.V. Fong & Mr. Zamzag - Bergstrom Paper Co.

²Personal communication between C.V. Fong & Mrs. Pell - Montveil Paper Co.

³Not available at the present time. Potlatch Corp. will forward this information in the future.

⁴Total annual cost is obtained from multiplying total annual production by annual unit cost.

⁵Assume 10% of the total U.S. tissue production is attributed to this category.

5.0 MODEL OF PCBs INVOLVEMENT IN THE PULP AND PAPER INDUSTRY

5.1 Purpose and Objectives of Model Development

Although it is generally agreed that the major input of PCBs into the paper industry has been through recycling of NCR carbonless copy paper (and this view is strongly supported by evidence presented previously in this report), there are a number of questions concerning PCBs in this industry which have not been answered:

- (1) How long will PCBs from NCR paper continue to cause significant product levels of PCBs?
- (2) How long will paper mill effluents continue to exhibit PCB levels of significance?
- (3) What are the chances for "hot spots" of PCB levels in products and effluents due to locally high concentrations of NCR paper in recycled fiber?
- (4) Are PCB levels in intake water significant at present in comparison to levels from NCR paper, with regard to product and effluent levels?

The purpose of developing and exercising a model of PCBs involvement in the paper industry was to obtain the best available answers to the above questions. By necessity, the model takes a simplistic material balance form; the major limitation of the utility and accuracy of the results obtained arises from the almost complete lack of data on process stream PCB levels and the extremely limited set of data concerning effluent and product concentrations of PCBs. However, the model does appear to be consistent with available information and does predict the PCB concentrations in various paper products and in the effluent water from paper processing plants in terms of the amount of input PCB accepted with the raw material and contained in the intake waters.

The effluent prediction is based on a constant distribution factor between the product and the effluent. Data available on sludge, effluent and products place this distribution coefficient in the vicinity of 1:1000, effluent

to product. The actual PCB concentration in the effluent entering the receiving stream will reflect the treatment process at a given site. With a more rigorous approach to the distribution coefficient, one would be able to narrow the limits of predictability considerably. We have aimed at the center of the array in order to maintain a tie to "average" conditions.

At all times it is realized that the model is only a general one; no attempt has been made to apply it to a particular mill. A simple mass balance calculation with known PCB inputs, water flows and production outputs would be a straightforward task for a given site.

The model does show that a mill which accepts NCR carbonless copy or converter scrap, has poor suspended solids removal and has a high PCB level in its intake water might be capable of producing a high PCB effluent as a local "hot spot". Present values for recycled wastepaper⁽⁶⁾ indicate this likelihood to be continually decreasing. However, the expected frequency or severity of hot spots cannot be fully addressed because of lack of data.

5.2 First Order Model of Paper Industry

5.2.1 Assumptions

The model is based upon the following assumptions:

- 1) The two primary sources of PCB to the paper industry are:
 - a) NCR carbonless copy paper made between 1957 and 1971 and its associated converter scrap at 3.4% PCBs by weight; and
 - b) The PCB load of the intake waters, taken to average 0.1 ppb.
- 2) A secondary source is PCBs already existing in recycled paper due to 1a and 1b above.
- 3) The routes of PCBs out of the paper industry are limited to:

- a) Product
 - b) Effluent
 - c) Sludge and other solid wastes (or process loss)
 - d) Evaporation
- 4) Most of the PCBs in the paper industry remain associated with the fiber, either as product or as sludge. This appears to be due to the presence of PCBs in microspheres used in the NCR paper plus the low solubility of PCBs in aqueous solution and its preferential association with surfaces and organic rich interfaces. In some cases PCBs found in industrial effluents are almost quantitatively associated with the suspended solids.
 - 5) Evaporative losses of PCB will depend to a great deal on the integrity of the capsular form. Industry experts have been quite unanimous in their agreement that capsular breakage would be small. The evaporative losses intimated by some of the mass balances attempted at the Institute of Paper Chemistry are very small compared to the amounts of PCB moving through the systems. As a result, we have chosen to neglect evaporative losses in the treatment of the model since any assessment would be fragmentary at best.
 - 6) Contributions of PCB by inks or adhesives are negligible and not considered to be large enough to affect even a locale distribution. Based on the estimation presented in Section 3.1, the upper bound of PCBs into paper products other than the NCR paper appears to be on the order of 50,000 to 100,000 pounds, much less than one percent of the total PCBs usage in the NCR paper during the same time frame. Thus, non-NCR PCBs should be negligible with regard to the model.

- 7) Prior to 1957, when NCR carbonless copy paper was introduced, the PCB content of paper products would have been controlled by the PCBs carried with the intake water. The effluent would have been cleaned by the passage of PCBs from the water to the fiber during the pulping and paper making process. Total transfer for a typical process would have produced a paper with a PCB concentration of 0.02 ppm. Based on this consideration, and the realization that present day detection limits for PCB in paper are in the vicinity of 0.1 ppm, the model has been exercised neglecting the intake water contribution.
- 8) The two routes for PCB return on NCR paper are:
 - a) As part of the recycling waste paper stream in "mixed" or deinked grades of paper stock.
 - b) As converter scrap purchased by mills that use it as furnish (raw material).

Other assumptions or specific decisions made in developing the model will be indicated at the point where the information is used or the equation described.

5.2.2 Model Structure

The first order model is an overview of the industry as a whole. Mass balance considerations are utilized to develop a "one-box" representation. Such a treatment avoids the complexity of the actual recycling web, and applies the limited data on PCB concentrations of waters, product and sludge to produce a first look at the time rate of change of PCB levels in average product as a result of the growth and eventual cessation of NCR carbonless copy paper in the recycled waste stream. This admittedly simple approach serves as a foundation upon which to further divide the industry, as well as providing a qualitative validation of many of the accepted descriptions of PCB occurrence within the industry.

Figure 5-1 shows a schematic representation of the first order paper industry model, where:

- $E(t)$ - evaporative losses of PCB. These losses are yet to be assessed on an industry wide scale, but early indications are that they are not dramatic. Any such losses would have the effect of lowering product, effluent and sludge PCB concentrations, but would not change the relationship between these.
- $V(t)$ - input of virgin wood pulp. Virgin wood has been found to be relatively free of PCBs, but may pick up some from the water used in the pulping stages.
- $W_{in}(t)$ - intake water. Census Bureau data for total water usage are relied on. The typical intake water PCB concentration is taken to be 0.1 ppb. This value is probably an upper bound on a natural water and nonetheless turns out to have only a small effect on PCB concentrations found in the paper industry.
- $S(t)$ - sludge output. This is the amount of process loss going to sludge. It is inferred that sludge output is proportional to the production rate and has the same concentration of PCBs as the product.
- $R(t)$ - amount of paper stock being recycled. The average lifetime of paper products is taken to be 1 year before recycling. Hence the concentration of PCBs in the paper stock is assumed to be that of the previous year's product.
- $W_{out}(t)$ - effluent water. It is generally held that PCBs in the effluent are strongly associated with the suspended solids. In the present case the effluent can be considered what might typically remain after primary treatment, removal of settleable solids and some suspended solids. How much removal occurs in an actual mill will depend on the type and amount of treatment available. It has been assumed here that the effluent PCB concentration is proportional to the product concentration. The constant of proportionality would depend on the treatment system efficiency for solids removal. But in

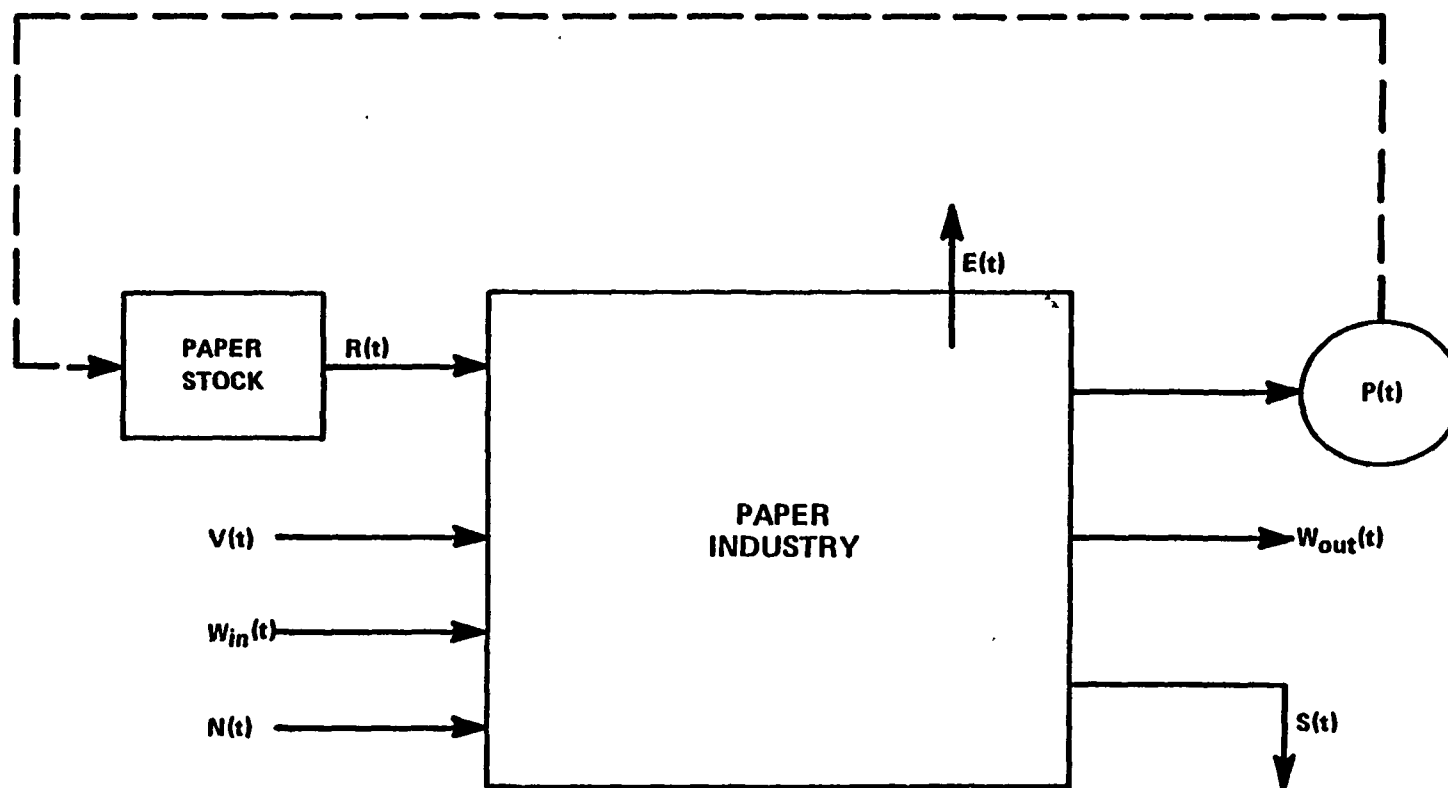


Figure 5-1. SCHEMATIC OF FIRST ORDER MODEL OF PAPER INDUSTRY

any case, the effluent concentration predicted by the model gives an idea of the PCB which might escape into the environment without further consideration and treatment.

- P(t) - annual production of the industry.
- N(t) - PCBs introduced to the paper industry as a result of NCR carbonless copy converter scrap and recycled used sheets. While NCR production figures for carbonless copy paper and its PCB content are known, the amount recycled from office and other commercial institutions or from converting operations can only be guessed at. Converter scrap varies between 10 and 15% (15% was the figure used in an A.D. Little Paper Industry study) for printing and writing grades.⁽²⁰⁾ However, much of this scrap was recycled in-plant, back into NCR carbonless forms - this amount could not be estimated by personnel at Mead (the manufacturers for NCR). Shade Information Systems, Inc., a converter of carbonless and a supplier of post-consumer office waste, in testimony before the Department of Natural Resources in Wisconsin, estimated that 10% of all office waste is presently recycled, that of this recycled paper, 10% came from old files and 90% from yearly usage, and that the average lifetime for files is three years.⁽²¹⁾

According to Mr. Ed Nastar of the International Business Forms Association, the major uses for carbonless paper are in invoices and customer statements with tax forms using a lesser amount. If one extends the Shade estimates to include commercial establishments like stores with offices then one can use the same estimates for carbonless paper: 10% of each years production is eventually recovered with 90% of that recovered coming from the previous year and the other 10% coming from old files with a three year half life. These estimates are used in the model. (To show the sensitivity of the model to the NCR recovery rate a 20% figure will be presented). Table 5-1 shows NCR production from 1957-1971.

Table 5-1
PCB Used in Carbonless Copy Paper

<u>Year</u>	<u>PCB in NCR Paper Manufactured (10⁴ Pounds)</u>
1957	58.7
1958	77.9
1959	101.9
1960	114.9
1961	164.3
1962	195.3
1963	228.1
1964	270.5
1965	348.9
1966	424.6
1967	435.5
1968	580.1
1969	627.8
1970	661.1
1971	126.6
1972	0
1973	0
1974	0
1975	0

Since the amount of old NCR carbonless recycled into the industry can only be estimated and few measurements on other than recycled box-board exist by which to validate the figures, the exact levels predicted by the model should be regarded with caution. Nonetheless, the model does reflect the trends and dynamics of PCB involvement in the industry.

The PCB mass balance equation for the First Order Model is written:

$$R(t)C_p(t-1) + N(t) + W_{in}(t)C_{w_{in}}(t) = P(t)C_p(t) + S(t)C_p(t) + W_{out}(t)C_{w_{out}}(t)$$

where:

- $C_p(t)$ \equiv PCBs concentration in product for year t.
- $C_{w_{in}}$ \equiv PCBs concentration in input water (taken to be 0.1 ppb)
- $C_{w_{out}}(t)$ \equiv PCBs concentration in effluent $\equiv \lambda C_p(t)$ where λ is a constant dependent on the level of suspended solids.

In EPA data (1, p. 84) the suspended solids are shown to range from 500 ppm in non-deinked paper mills to 1700 ppm in deinking effluents. Considering that the best available technology is not uniformly used now or in the past, 1000 ppm is assumed for a suspended solids load, and the model is exercised with λ at $\frac{1}{1000}$. From John Strange Paper Co. data a λ of $\frac{2}{1000}$ was obtained while Ft. Howard information indicated λ at $\frac{1.1}{1000}$ to $\frac{1.2}{1000}$.

and: $S(t)$, the sludge output is taken to be proportional to $P(t)$. That is:

$$S(t) = \xi(t), \text{ where } \xi \text{ is the proportionality constant.}$$

A value of 4.5% was chosen for ξ , based on previously reported data for process losses. (22)

Rewriting the previous equation,

$$R(t)C_p(t-1) + N(t) + 10^{-10}W_{in}(t) = C_p(t) \left[\underbrace{0.955}_{1-\xi} P(t) + \underbrace{10^{-3}}_{\lambda} W_{out}(t) \right]$$

As a simplistic first exercise - assume $\lambda = 0$, i.e., all PCB is retained by the product. Let the $N(t)$ assume three cases:

A_I - 10% recovery

A_{II} - 15% recovery (10% recycle + 5% converter scrap)

A_{III} - 25% recovery (20% recycle + 5% converter scrap)

Figure 5-2 shows the PCB concentration in the product for these three different recovery rates. The NCR production is also plotted as a reference to show the roll-off of the curves.

Immediately obvious is the direct and quantitative relation between the NCR recovery and PCBs in the product. Product levels rapidly fall below the 1 ppm level by 1973 or 1974, so that input water concentrations ($W_{in}(t)$) appear to be completely dominated by the NCR contribution.

Further insight is gained if the data of A_{II} (15% recovery) are plotted again with $R(t) = \text{zero}$; that is, if there was no recycling of product back into the paper stock input. Figure 5-3 shows the result of this exercise. For the overall industry under these conditions, 15% NCR recovery appears to be responsible for about 83% of the PCB in the product. However, if broken down further, specific segments of the industry which utilize a large proportion of wastepaper in their furnish would be expected to exhibit a larger dependence on the PCBs recycling to the paper stock input.

The effect of process loss to sludge is easily demonstrated in a tabular format. Table 5-2 shows the 15% NCR recovery data now allowing $R(t)$ to operate (i.e., recycling to paper stock) and λ values of 0 (plotted in Figure 5-2), 10^{-3} , and 2×10^{-3} . According to the data on Table 5-2, a λ of 10^{-3} (ratio of PCBs level in effluent to TSS level in effluent) decreases the PCBs levels in the product by only about ten percent from those at zero PCBs in the effluent ($\lambda = 0$). A further reduction of six to ten per cent in product PCB levels results from application of $\lambda = 2 \times 10^{-3}$. As further internal reuse schemes for white water proliferate a continuing decrease would be expected in both suspended solids and λ . All peripheral factors point to a continuing association of the majority of PCBs introduced into the system with the product.

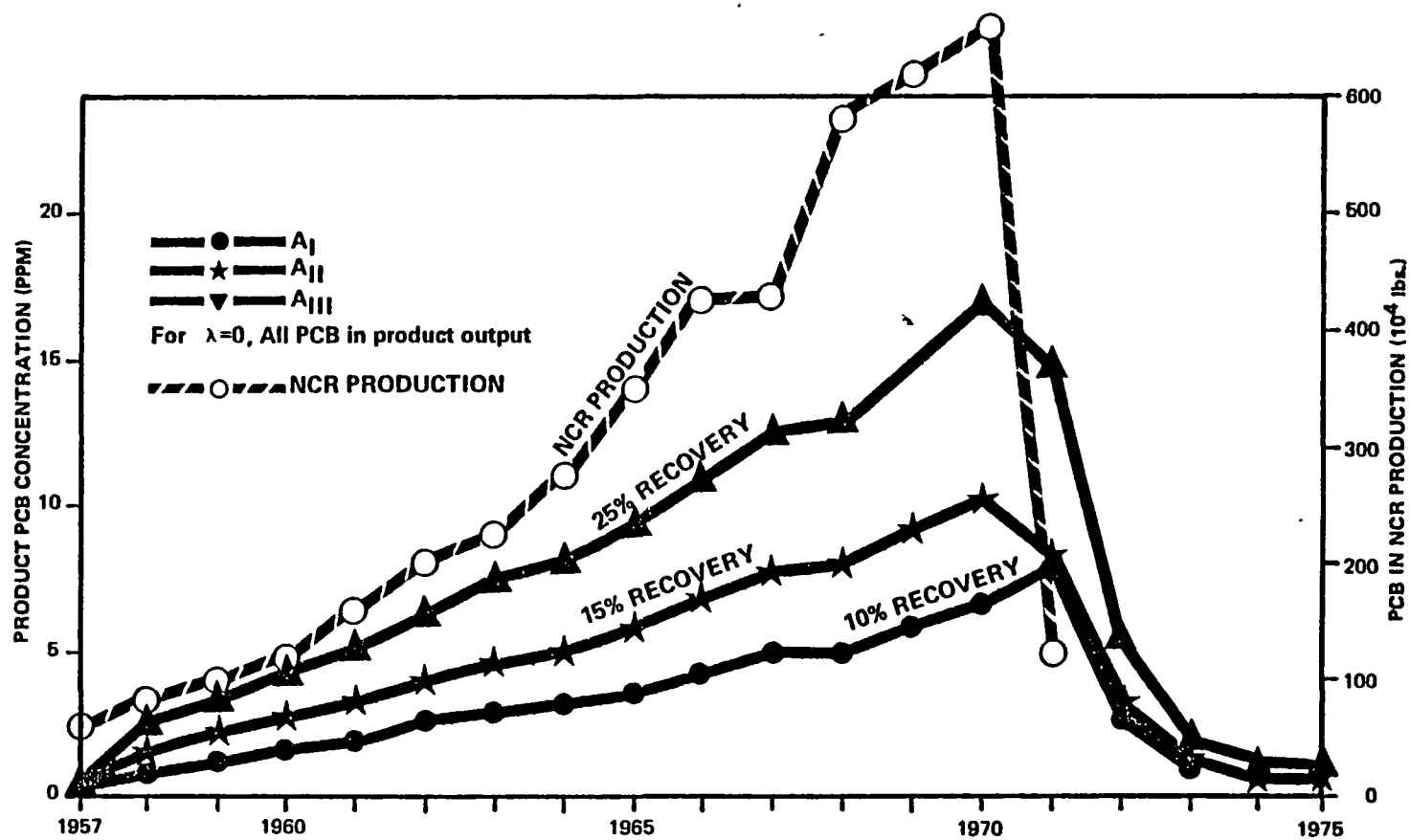


Figure 5-2. FIRST ORDER MODEL WITH DIFFERING RECOVERY RATE FOR RECYCLED PAPER

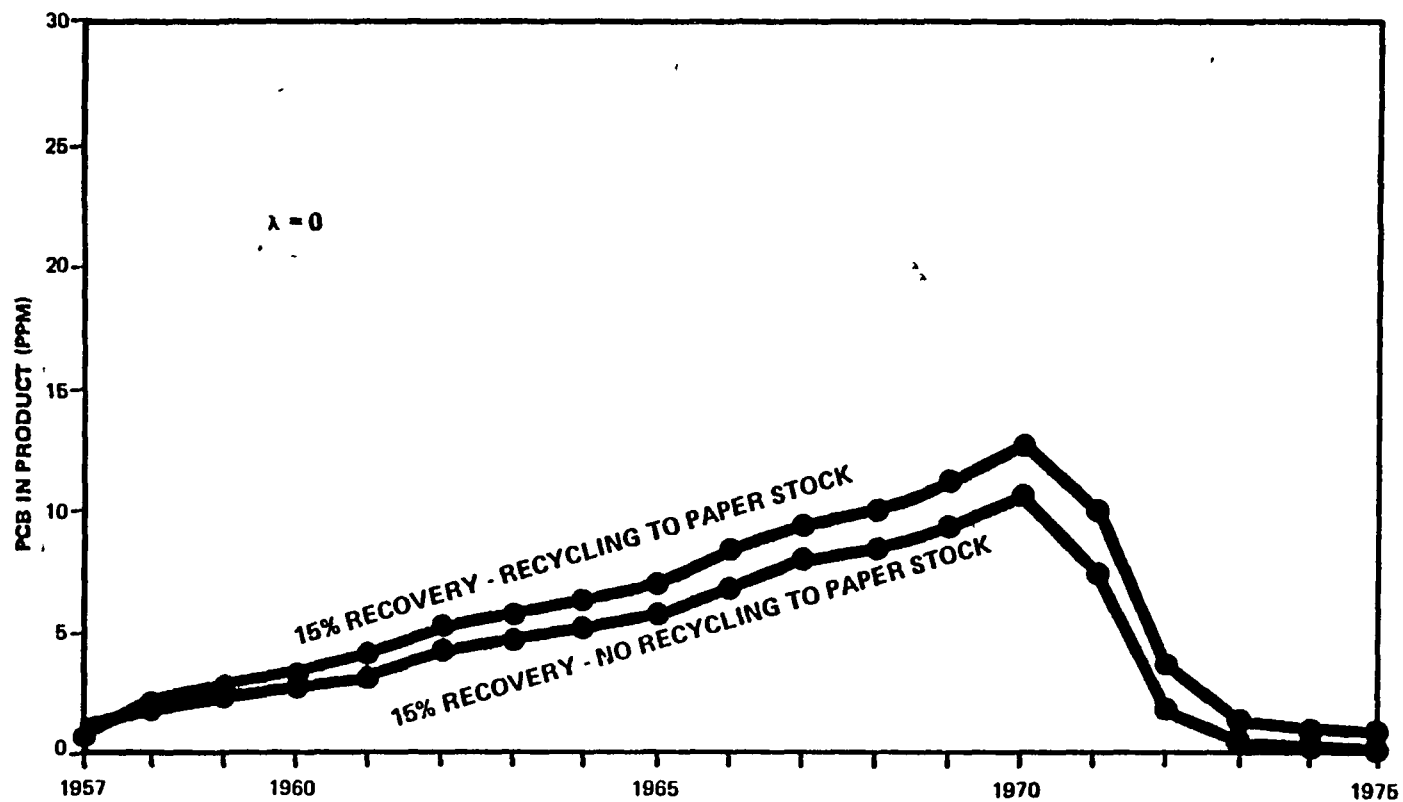


Figure 5-3. AFFECT OF RECYCLING PAPER OTHER THAN NCR CARBONLESS PAPER ON PCB CONTENT OF FIRST ORDER MODEL PRODUCTION

Table 5-2
PCB Concentration in Product (ppm)

<u>Year</u>	<u>$\lambda=0$</u>	<u>$\lambda=10^{-3}$</u>	<u>$\lambda=2 \times 10^{-3}$</u>
1957	0.48	0.43	0.39
1958	1.58	1.41	1.27
1959	2.15	1.93	1.75
1960	2.66	2.39	2.16
1961	3.20	2.88	2.62
1962	3.96	3.58	3.26
1963	4.58	4.15	3.79
1964	5.04	4.59	4.20
1965	5.68	5.28	4.85
1966	6.76	6.21	5.72
1967	7.69	7.04	6.49
1968	8.08	7.42	6.86
1969	9.18	8.46	7.85
1970	10.20	9.40	8.72
1971	8.03	7.40	6.86
1972	2.83	2.61	2.43
1973	0.86	0.80	0.74
1974	0.45	0.42	0.39
1975	0.33	0.30	0.28

This general overall look at PCBs demonstrated the following:

- a) A 1970-71 peak in product PCB concentrations corresponding to maximum PCB usage in NCR paper plus a one-year or less delay in reaching maximum PCB levels in the recycling stream.
- b) With the cessation of NCR production the drop off in product PCB was rapid. Different specific industry segments would show a different drop off rate (this is investigated with the second order model).
- c) Using reasonable choices for the adjustable constants, the major source of PCB is the NCR carbonless paper's direct input to the industry. Further recycling of paper contaminated by recycled NCR input has a relatively small effect on the concentration observed in the paper product.
- d) It is difficult to assess the quantitative effects of such industry responses to the PCBs problem as elimination of deinking grades as furnish for food board. There is no doubt that within a specific segment of the industry such activity was beneficial. In the overview of the first order model, however, these effects cannot be separated out. The model as developed exhibits an overwhelming response to the NCR carbonless recovery rate which would inundate any analysis of a finer internal structure.

5.3 Second Order Model of Paper Industry

5.3.1 Industry Categorization for Second Order Model

The obvious industry categorization useful to a more detailed industry analysis is paperboard; paper; and construction paper and board. The latter segment includes portions which use 100% recycled paper stock (construction paper) and others which use little, if any, recycled paper stock (construction board) and can be further subdivided on this basis. Figure 5-4 shows schematically

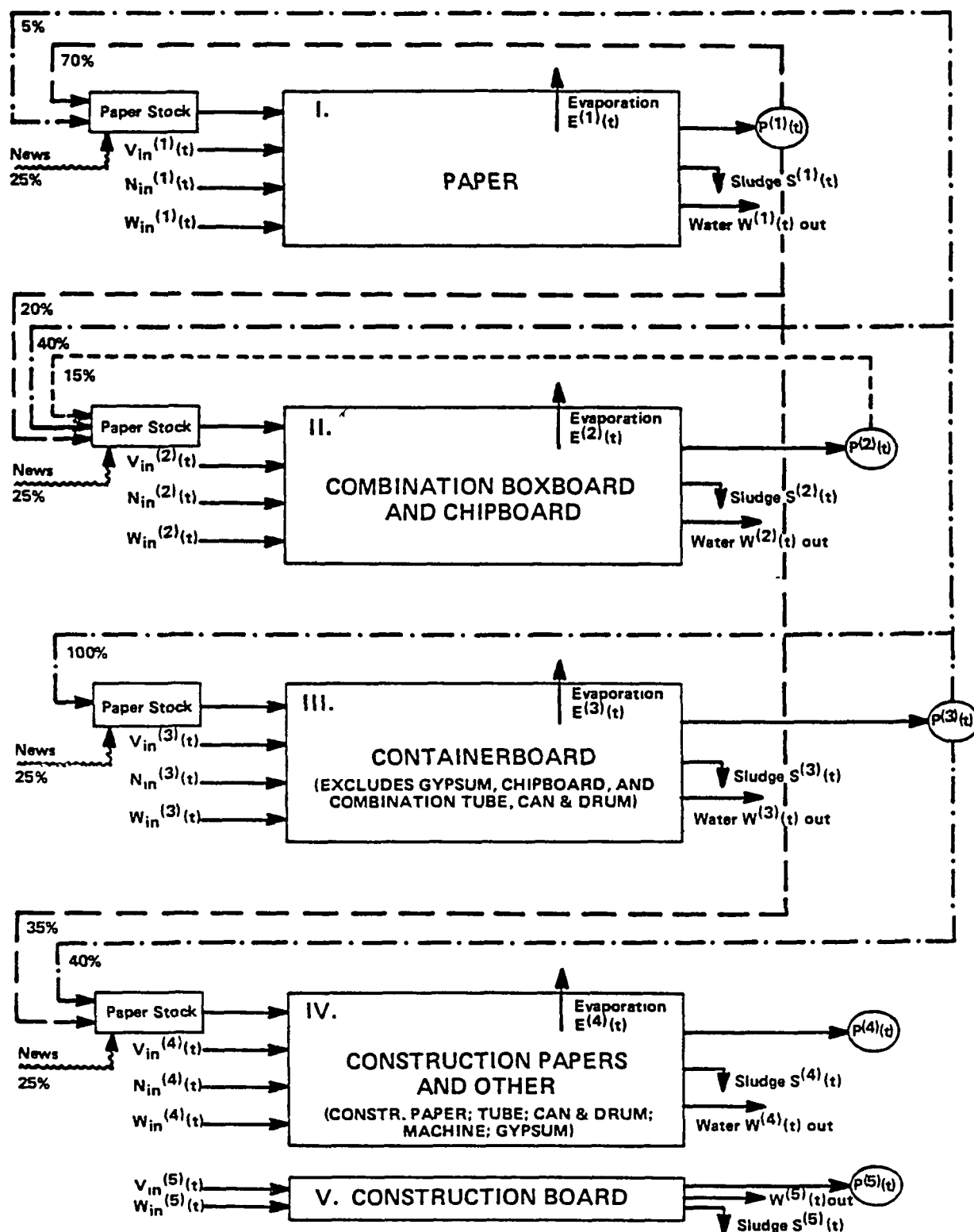


Figure 5-4. SCHEMATIC OF SECOND ORDER MODEL

the five categories selected and the flows of products returning to these industry segments in recycled waste streams as well as other inputs, products, and discharges. Figure 5-4 is thus essentially a schematic diagram of the second order model. Annual production data from 1957 through 1974 for each of the five industry segments are presented on Table 5-3.

Segment I, paper, has a product output approximately equal to the sum of segments II, III, and IV. This should be remembered when one assesses the total load of PCB associated with the production of a given segment. The load will be PCB concentration times the output.

Segment II, combination boxboard and chipboard, is based on a raw material which is 100% recycled. Historical PCB data (back to 1971) exists for combination boxboard. Almost all of the deinked paper stock (ledger grades) went into box production prior to 1971; also, most of the mixed grades and pulp substitutes went into box production. As a result, most NCR paper entering the general area of paperboard would probably wind up associated with combination boxboard and chipboard. Chipboard is included since sufficient data were available on this category, ⁽²³⁾ but chipboard is less than 10% of this segment's total output.

Segment III contains those items which are primarily made from virgin wood or recycled product from Segment III.

Segment V, construction board, uses all virgin wood and is not recycled.

Segment IV is a composite segment, the components of which have the following characteristics:

- a) All use a high percentage of mixed waste which could contain NCR sheets.
- b) Many products are used in building applications which precludes their entry into the recycled waste stream.
- c) The tube, can and drum component is not likely to be recycled, though it has an open usage different than the building materials.

Table 5-3
Annual Production for Industry Segments (10⁶ tons)

<u>Year</u>	<u>I Paper</u>	<u>II Combination Boxboard & Chipboard</u>	<u>III Containerboard</u>	<u>IV Construction Papers and Others</u>
1957	13.6	3.9	8.9	2.7
1958	13.5	4.0	8.8	2.8
1959	15.0	4.2	9.8	3.1
1960	15.4	4.2	10.3	2.8
1961	15.7	4.3	10.9	3.0
1962	16.5	4.3	11.6	3.1
1963	17.3	4.4	12.2	3.2
1964	18.2	4.5	13.4	3.4
1965	19.2	4.7	14.4	3.5
1966	20.7	5.0	15.9	3.3
1967	20.9	4.1	16.5	3.1
1968	22.4	4.4	18.4	3.5
1969	23.6	4.3	20.0	3.5
1970	23.6	4.1	19.7	3.5
1971	23.8	3.8	20.3	4.0
1972	25.4	3.9	22.4	4.3
1973	26.5	4.0	23.3	4.3
1974	26.9	3.5	22.2	4.2

5.3.2 Equations

The same definitions of mathematical terms hold for the second order model as for the first order model (see Sec. 5.2.2), applied on a segment-by-segment basis. In addition, the second order model uses superscripts to denote association with a particular industry segment. Other symbols used are:

$C_v^{(1)}(t) \equiv$ PCB concentration of virgin wood in industry segment 1.

$C_e^{(1)}(t) \equiv$ PCB concentration in aqueous solution of effluent from segment 1.

The following are based on our assumptions:

$$C_v^{(1)}(t) = C_v^{(2)}(t) = C_v^{(3)}(t) = C_v^{(4)}(t) = C_v^{(5)}(t) \equiv 0$$

$$C_{win}^{(1)}(t) = C_{win}^{(2)}(t) = C_{win}^{(3)}(t) = C_{win}^{(4)}(t) = C_{win}^{(5)}(t) \equiv 0$$

$$E^{(1)}(t) = E^{(2)}(t) = E^{(3)}(t) = E^{(4)}(t) = E^{(5)}(t) \equiv 0$$

and,

$$\left. \begin{aligned} C_{wout}^{(1)}(t) &\equiv \lambda_1 C^{(1)}(t) \\ C_{wout}^{(2)}(t) &\equiv \lambda_2 C^{(2)}(t) \\ C_{wout}^{(3)}(t) &\equiv \lambda_3 C^{(3)}(t) \\ C_{wout}^{(4)}(t) &\equiv \lambda_4 C^{(4)}(t) \\ C_{wout}^{(5)}(t) &\equiv \lambda_5 C^{(5)}(t) \end{aligned} \right\} \quad \text{where } \lambda \text{'s are constants.}$$

Since newsprint contains little if any PCB,

$$N^{(3)}(t) \equiv 0$$

$$N^{(5)}(t) \equiv 0$$

Prior to 1957,

$$C_p^{(1)}(t) = C_p^{(2)}(t) = C_p^{(3)}(t) = C_p^{(4)}(t) = C_p^{(5)}(t) \equiv 0$$

After 1957 one has these 5 unknowns, and the following 5 equations:

$$(1) \quad N^{(1)}(t) + \left[.70R^{(1)}(t)C_p^{(1)}(t-1) + 0.05R^{(1)}(t)C_p^{(3)}(t-1) + .25R^{(1)}(t)(0) \right] \\ = \left[P^{(1)}(t) + S^{(1)}(t) + \lambda_1 W_{out}^{(1)}(t) \right] C_p^{(1)}(t)$$

$$(2) \quad N^{(2)}(t) + \left[0.15R^{(2)}(t)C_p^{(2)}(t-1) + 0.20R^{(2)}(t)C_p^{(1)}(t-1) + \right. \\ \left. 0.40R^{(2)}(t)C_p^{(3)}(t-1) + 0.25R^{(2)}(t)(0) \right] \\ = \left[P^{(2)}(t) + S^{(2)}(t) + \lambda_2 W_{out}^{(2)}(t) \right] C_p^{(2)}(t)$$

(This holds until 1971 at which time the paperboard segment greatly decreased their usage of recycled paper. Thus, the coefficient of 0.20 for the paper portion of the paper stock input is taken to be zero for years after 1971.)

$$(3) \quad \left[R^{(3)}(t)C_p^{(3)}(t-1) \right] = \left[P^{(3)}(t) + S^{(3)}(t) + \lambda_3 W_{out}^{(3)}(t) \right] C_p^{(3)}(t)$$

$$(4) \quad N^{(4)}(t) + \left[0.35R^{(4)}(t)C_p^{(1)}(t-1) + 0.40R^{(4)}(t)C_p^{(3)}(t-1) + 0.25R^{(4)}(t)(0) \right] \\ = \left[P^{(4)}(t) + S^{(4)}(t) + \lambda_4 W_{out}^{(4)}(t) \right] C_p^{(4)}(t)$$

$$(5) \quad 0 = \left[P^{(5)}(t) + S^{(5)}(t) + \lambda_5 W_{out}^{(5)}(t) \right] C_p^{(5)}(t)$$

Notes:

(a) From equation (5) $C_p^{(5)}(t) = 0$ for all (t) .

(b) From equation (3), $C_p^{(3)}(t) = 0$ for all (t) .

(c) All λ 's are from .001 to .002. This allows us to ignore λ terms since they are so much smaller than the $P(t)$ and $S(t)$ terms.

Substitution yields:

From equation (1)

$$N^{(1)}(t) 0.70 C_p^{(1)}(t-1) R^{(1)}(t) = [P^{(1)}(t) + S^{(1)}(t)] C_p^{(1)}(t)$$

From equation (2)

$$N^{(2)}(t) + [0.20 C_p^{(1)}(t-1) + 0.15 C_p^{(2)}(t-1)] R^{(2)}(t) = [P^{(2)}(t) + S^{(2)}(t)] C_p^{(2)}(t)$$

(The 0.20 constant drops to 0 after 1971 as noted above)

From equation (4)

$$N^{(4)}(t) + 0.35 R^{(4)}(t) C_p^{(1)}(t-1) = [P^{(4)}(t) + S^{(4)}(t)] C_p^{(4)}(t)$$

Equations (3) and (5) are negligible, based on Notes (a) and (b) above.

5.3.3 Quantitation and Exercise of the 2nd Order Model

McLenahan's study of 1969-1970 paper stock usage was used as the basis for quantitating the model.⁽²³⁾ This extensive study accounted for over 90% of the wastepaper stock usage. It also tabulated the paper stock by type and associated that with its end use. A number of other studies have since been based on these figures; utilization of these data thus keeps the model on a somewhat parallel footing for comparison with the other studies.

The second order model is a good deal more complex than its predecessor in Section 5.2. To explore the effects of recycling on specific segments of the industry it was necessary to subdivide the industry into identifiable sectors. This necessitated developing a reasonable set of criteria for routing the recycled paper between these sectors.

The following additional assumptions were made:

- 1) Paper products produced one year are considered to be recycled the next.
- 2) The paper stock percentages of various inputs were taken to be constant over the period 1957 to 1974, except in the combination boxboard and chipboard category after 1970. In this category, industry reaction to PCB in food packaging and the eventual FDA 10 ppm limit is reflected.
- 3) Each segment's percentage of the overall paper stock usage is constant from 1957 to 1974 using the 1969 percentage. The model is quite insensitive to changes in this parameter.
- 4) Recycled newsprint is considered to be PCB free. Newsprint is produced primarily from virgin fiber, and the only paper stock used in newsprint is other newsprint. Consequently, no PCB from NCR paper should be introduced into this segment. Measurements by Hazleton Laboratories in 1972 confirm low background values of PCBs in newsprint.⁽⁹⁾

Since newsprint is only a small percentage of paper output it was not set aside as a separate category. However, newsprint is a sizeable fraction of the recycled waste stream and here it was accounted for separately.

- 5) Containerboard uses very little paper stock, and what it does use is old containers or container clippings. (This excludes gypsumboard, chipboard, and recycled tube, can and drum segments). We therefore approximated paper stock in this subcategory to be 100% container. This implies that containerboard will be PCB free.
- 6) As before, process loss to sludge was assumed to have the same PCB concentration as the product. The process loss estimates are those previously published for 1970.⁽²²⁾
- 7) Bureau of Census data was used to obtain values for total paper stock recycled.
- 8) The model is very sensitive to the total amount of NCR carbonless copy paper recycled into the industry, and to its distribution within the industry. Uncertainties in these affect the details of the model, but not the general trends.

- 9) Virgin wood contains negligible PCB.
- 10) PCB concentration of input waters is taken to be 0.1 ppb.
- 11) Evaporative losses are not considered for the reasons given for the first order model exercise in Section 5.2.
- 12) The "mixed" category of waste paper includes #1 and #2 mixed, super mixed, boxboard clippings and mill wrappers. The amounts of each going into "mixed" in 1969 was investigated by other workers.^(20,23) Paper stock dealers interviewed indicated that "mixed" paper was usually office waste with the following approximate composition:

	<u>Range (%)</u>	<u>Chosen for Model</u>
Old Corrugated Cartons	0-15	10
Newsprint	10-25	20
High-Grade Printing & Writing	60-90	70

- 13) The loss of PCBs in solution in effluent waters is assumed to be negligible compared to PCBs associated with the suspended solids.

The model is exercised for two distribution schemes for NCR paper as follows:

- a) The NCR received in a given year is assumed to be 5% of the converter scrap from that year's production and 10% of the post consumer wastepaper. Of the post consumer waste 9/10 came from the previous production year and 1/10 came from years prior to that.

(A three year half-life with exponential decay is postulated for the post consumer waste NCR paper which is recycled more than 1 year after being produced. This assumption is significant only after 1971.)

All of the 5% NCR converter scrap is assumed to go into the paper segment of the industry. The combination boxboard segment rejected it due to a discoloration problem.

The recovered post consumer NCR was distributed according to the percentage of printing and writing paper being recycled within each segment. 70% of

the mixed category was taken to be printing and writing paper except within boxboard paper stock where it is estimated that 50% of the mixed was actually boxboard clippings. About 2/3 of the deinking category is taken to be printing and writing paper. The final breakdown of NCR in the paper stock for each segment thus becomes:

PAPER - 5% converter scrap

3% post consumer

COMBINATION BOXBOARD AND CHIPBOARD - 3.5% post consumer

CONSTRUCTION PAPER - 3.5% post consumer

After 1970 the combination boxboard segment drastically reduced the use of ledger grade papers and some pulp substitutes. This was industry's response to eliminate NCR from inadvertently contaminating the foodboard grades. In the model, the NCR entry figures for that segment are adjusted to reflect this industry action. The NCR going into the paper segment may have increased its percentage of NCR received as a result. Though this is not entirely clear, it has been included in the second exercise of the model.

Figure 5-5 shows the response of the model. The rapid decrease in segment II PCB levels after 1970 is evident. Concomitant reductions occur in segments I and IV. While the latter two reflect the loss of the NCR carbonless copy paper production, the former shows cessation of PCBs usage by NCR as well as additional reduction caused by the industry action.

A second exercise of the model, shown on Figure 5-6, is made on the assumption that 10% of the returning NCR is sent to the paper and boxboard segments based on the use of deinking stock. The paper segment has not used mixed grades and boxboard officials state that their product has not used mixed grades, although several references indicate some usage.^(20,23) The second exercise is performed with the assumption that the boxboard segment (II) does not use mixed grades, other than boxboard clippings.

10% recovery of wastepaper is calculated at 9% the year after production, and 1% thereafter based on the 3 year half-life described earlier.

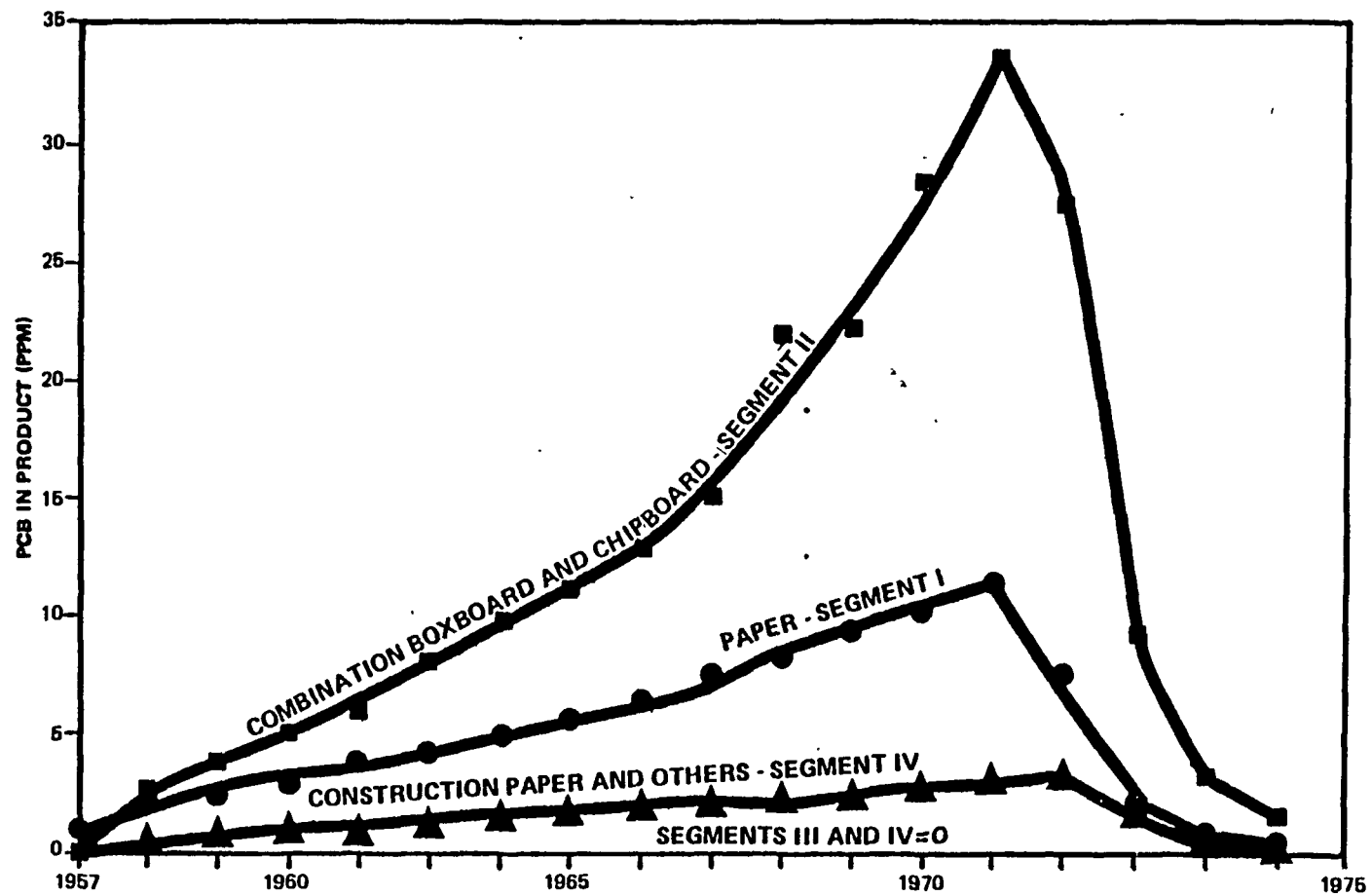


Figure 5-5. FIRST EXERCISE OF SECOND ORDER MODEL

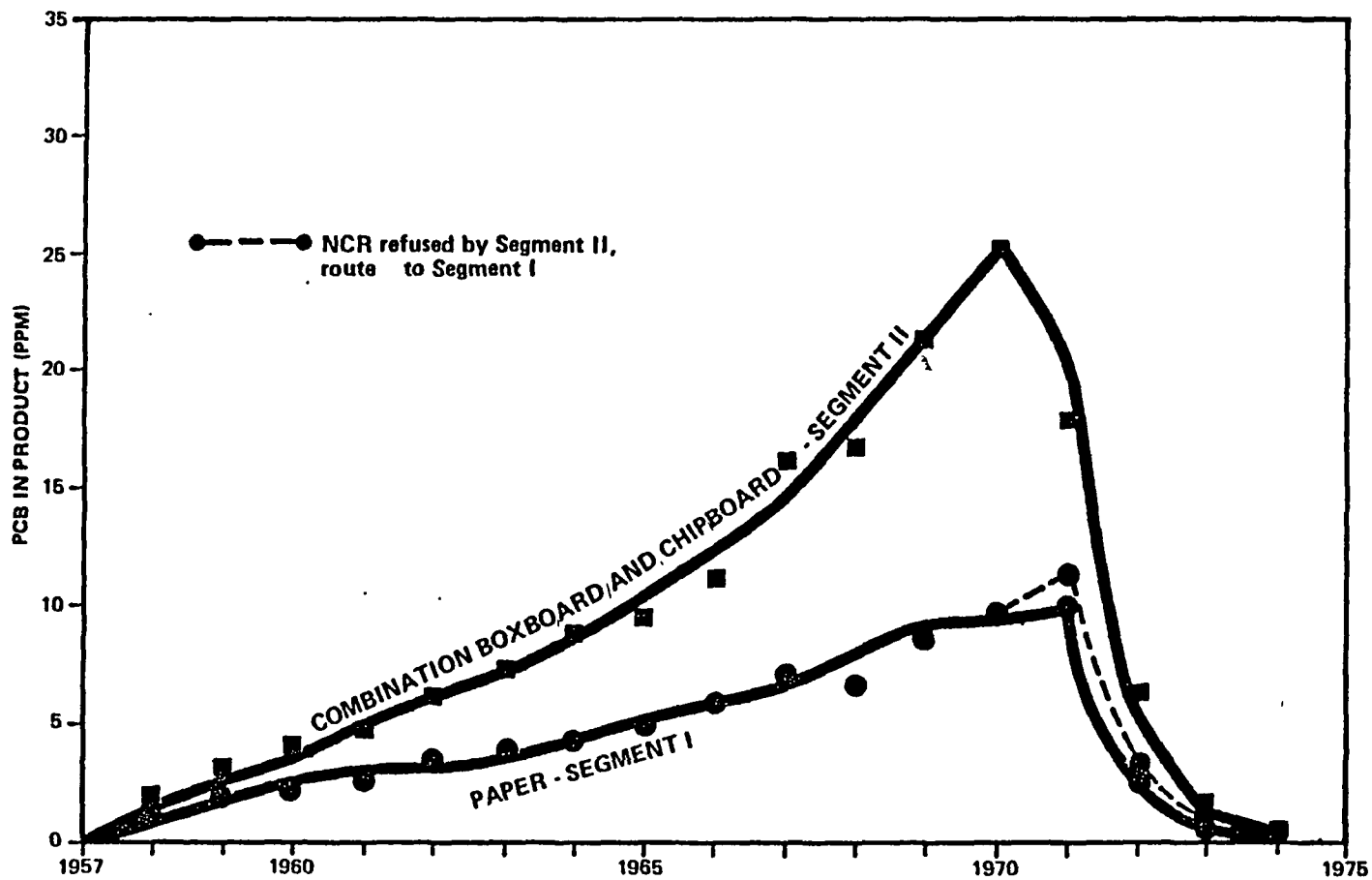


Figure 5-6. SECOND EXERCISE BY SECOND ORDER MODEL

The post-1970 reduction of NCR into the combination boxboard segment is included. The reduction in ledger grade usage by boxboard is assumed to have been by half in 1971 and complete stoppage thereafter. If the ledger stream might have diverted to the paper segment upon its rejection by the boxboard (segment II), the effect this would have had on the paper PCB is shown by a dotted plot from 1971 on in Figure 5-6.

Overall, we see the same general trends in both exercises (Figures 5-5 and 5-6). The routing chosen for the returning PCB in the NCR paper effects the details of the product concentrations, as does the relative size of the production output within each segment.

In each scenario, the primary removal of PCB containing NCR from production allowed a return of every segment to pre-1957 PCB levels in the products by 1974 or 1975. This trend is reflected in the decreases shown by available data in Table 3-2. The decreases documented are of the same general magnitude as produced by the model. Data on "recycled wastepaper input"⁽⁶⁾ has reflected a drop to 0.15 ppm in 1976, which is near the detection limit of the analysis for PCB in paper products.

5.4 Discussion of Model Results

The results obtained from exercising the model show clearly the overwhelming dependence of PCB levels in both product and effluents upon the NCR paper content of recycled fiber. According to these results, product levels of PCBs resulting from the NCR paper should be less than one ppm by the present time (1976) with the possible exception of the combination boxboard and boxboard segment, and of course, excepting localized hot spots caused by inclusion of small amounts of NCR paper in the fiber recovery stream. This result agrees with recent analytical results on PCB levels in paper industry products. Product levels, effluent levels, and frequency and severity of hot spots should continue to decline slowly as the PCBs in paper products are diluted further with virgin and less contaminated secondary fiber.

The ratio of PCBs concentration to TSS in the effluents had little effect on product levels, as would be expected. Values of this ratio in the range of

0.001 to 0.002 appear to be consistent with available data on both effluents and products. This result indicates that most of the PCBs entering the process exit in the product and thus generally agrees with the analysis of Section 3.

The overall agreement of the results obtained with the model tend to support the various assumptions made. Agreement is reflected by comparison with available data on both product and effluent PCB levels. Thus, the model as presented does appear to represent a reasonable and consistent material balance for PCBs around the paper industry.

A distribution for incoming PCBs between product, effluent, and waste treatment sludge can be calculated based on the results of the model. Using the following values:

- (1) PCBs level on product = 1 ppm of solids
- (2) PCBs on solids in wastes = 2 ppm of solids
- (3) 90 percent removal of solids and PCBs in wastewater treatment
- (4) 135 ppm suspended solids in final effluent
- (5) 0.27 ppb PCBs in final effluent
- (6) Zero loss through vaporization

The results obtained are:

<u>Plant Stream</u>	<u>Percentage of Incoming PCBs Contained Therein</u>	<u>Weight of Stream*</u>	<u>PCBs Level in Stream</u>	<u>Solids Content</u>
Product	75-80	1 kkg	1 ppm	95-96%
Sludge	18-20	0.6 kkg	0.4 ppm	20-30%
Effluent	2-3	100 kkg	0.27 ppb	135 ppm

* Based on one kkg of product.

The results obtained indicate that on the order of 75 percent of the PCBs entering a paper mill exit associated with the product. The values selected probably represent more of a "best case" situation for a recycling plant than a typical situation within the industry. The PCBs distribution should vary from plant to plant and from product to product, but should not be nearly so widely variable as suspended solids or PCBs concentrations, which are known to fluctuate widely from day to day in a given plant.

6.0 CONCLUSIONS

The following conclusions are based on the evidence presented in this report:

- (1) The recycling of NCR carbonless copy paper was and still is the only major source of PCBs into the paper industry.
- (2) PCB levels in paper products have been decreasing since 1972 and apparently will continue to decrease under the influence of continued dilution of PCBs from recycled NCR paper.
- (3) PCB levels in effluents from paper mills utilizing reclaimed fiber have been decreasing in recent years, and will continue to decrease, due to decreased PCB levels in reclaimed fiber plus application of wastewater treatment technology.
- (4) PCB levels in sludges resulting from wastewater treatment may be as high as 10 - 20 ppm. Disposal of such material should be performed with care.
- (5) Application of carbon adsorption as an end-of-pipe method for PCBs removal from wastewater in the paper recycling industry could increase product prices as much as three to five percent.
- (6) The proportions of PCBs present in intact microballoons in paper products and in paper industry wastewaters are not known. General indications are that more PCBs in the industry are encapsulated than are "free" (released from microballoons plus other sources).
- (7) The model generated to define PCBs involvement in the paper industry represents a reasonable and consistent material balance of PCBs input and output in this industry.
- (8) According to the model, PCB levels in products and effluents are sensitive only to the parameters associated with recycle of NCR carbonless copy paper containing PCBs.

- (9) The product PCB levels obtained from exercise of the model agree well with available data; the results indicate a steep drop-off following cessation of PCBs usage by NCR and a continuing, but less steep, decrease thereafter. Current product levels are in the one ppm range (recycled fiber).
- (10) Within the limitations and assumptions of the model, on the order of 75 percent of the PCBs entering the papermaking process exit associated with the products.

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DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS
AND PROCESS STREAMS

KEY WORDS:

Polychlorinated biphenyls, Analytical methods, Chemical analysis,
Cellulose fibers, Effluents, Reclaimed fibers, Paper mills,
Gas chromatography, Volatilization, Stability, Storage

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ABSTRACT

Special techniques have been found necessary for isolating PCB's from cellulose fiber-containing effluents and process streams and for determining PCB's in effluents from paper mills using recycled fiber. Sources of potential PCB loss from aqueous solutions are revealed and means of avoiding these losses are proposed.

Significant amounts of PCB remained on cellulose fibers following separatory funnel extraction of a fiber-water suspension with hexane or methylene chloride-hexane. Reflux of the fibers with alcoholic KOH was necessary to remove the remaining PCBs. PCB losses due to volatilization from aqueous solution occurred during analysis, but the

were minimized by working in a cool environment and covering the sample with a layer of hexane. The presence of cellulose fibers in PCB-containing effluents enhanced the effluents' stability during storage.

Chromium trioxide oxidation was found to be valuable in cleaning up extracts from paper mill effluents. Perchlorination is apt to yield misleading results.

INTRODUCTION

Polychlorinated biphenyls (PCB's) are commonly determined in industrial effluents by a method involving liquid-liquid extraction, Florisil cleanup, and electron capture gas chromatography, as prescribed by the U.S. Environmental Protection Agency¹. The utility of this and other methods was evaluated for use on paper mill effluents and process streams within the mill.

ISOLATION OF PCB'S FROM FIBER-WATER SUSPENSIONS

Known amounts of Aroclor 1242, 100 µg/l., were added to 1% suspensions of cellulose fibers in water. Incomplete recoveries were experienced when these suspensions were subjected to triple separatory funnel extractions with petroleum ether, hexane, or 15% methylene chloride in hexane. Following the separatory funnel extraction, the fibers were filtered from the sample and the residual PCB was removed from the fibers by reflux in 2% alcoholic KOH, as is normally used for determining PCB's in paperboard.² Removal of all residual PCB by the alcoholic KOH was demonstrated by dissolving the fibers in 72% H₂SO₄, diluting with water, and extracting with hexane.

Data in Table 1 resulted from a study designed to determine whether alcoholic KOH reflux of the fibers subsequent to separatory funnel extraction was needed to remove PCB's from fiber-water suspensions with low fiber contents. The results indicate that fibers, even at low concentrations in the sample, retained some PCB's, and that alcoholic KOH reflux was needed for complete PCB removal. However, in analysis of effluents containing less than 0.01% suspended hardwood fibers, the amount of PCB retained by the fibers was small compared with other reported sources of error in PCB determinations (e.g., 20% relative standard deviation for chromatogram quantitation³). Somewhat smaller amounts of Aroclor 1242 were retained by softwood fibers.

Thus, it may be concluded that the EPA liquid-liquid extraction technique should be adequate for most effluents containing low amounts of suspended solids and that it is inadequate for fiber-water suspensions within the mill. Because of their high suspended

TABLE 1

Recovery of Aroclor 1242 from Hardwood Fiber Suspensions

Fiber Content, %	Recovery by Extraction, %	Recovery from Fibers, %	Total Recovery, %
0.005	97.0	0.9	97.9
0.01	96.4	2.4	98.8
0.05	91.8	8.4	100.2
0.10	91.8	10.8	102.6
0.16	84.2	9.0	93.2
0.40	80.2	15.8	96.0
0.60	80.0	15.5	95.5
0.80	80.4	15.6	96.0

solids contents, the fiber-water suspensions require a separate alcoholic KOH reflux to remove all of the PCB's from the fibers.

MINIMIZING PCB LOSSES DUE TO VOLATILIZATION

Low recoveries (60-80%) of known amounts of Aroclor 1242 added to aqueous samples were experienced in the summer. Volatilization of PCB's from aqueous solution, as described by Mackay and Wolkoff⁴ and Paris, *et al.*⁵, during analysis of the samples seemed to be a possible explanation for the low values. Trapping of the Aroclor 1242 from the gas phase, as shown by the data in Table 2, demonstrated that volatilization could occur from aqueous solutions and fiber-water suspensions. A stream of nitrogen entered through a stopper in the top of a suction flask, impinged upon (but did not bubble through) the sample, and exited via the side arm of the flask into a trap containing deactivated Florisil.⁶

TABLE 2

Volatilization and Trapping of Aroclor 1242

Sample	Start, μg	Remaining, μg	Trapped, μg
Aqueous solution	10	4.0	3.9
Softwood suspension	10	5.8	2.9

Conditions: One hundred ml solution or 0.5% fiber-water suspension in 125-ml suction flask. N₂ flow: 600 ml/min across surface for 2 hours at 23°C. Trap: 0.3 g deactivated Florisil in 5 mm glass tube.

Losses of Aroclor 1242 from fiber-water suspensions in stirred beakers under simulated summer and winter laboratory conditions are shown in Table 3. A comparison of total recoveries from the open, cool (Condition B) and open, warm (Condition D) samples suggests that Aroclor 1242 was lost by volatilization during 5 minutes stirring under summer conditions but not under winter conditions. It may be speculated that PCB loss from the closed, warm beaker (Condition C) occurred because the aluminum foil cover formed an imperfect seal or that some PCB escaped into the air space between the foil and the solution.

These studies have provided the basis for the recommendations listed below for minimizing PCB volatilization losses during sample handling and analysis:

1. Minimize air space in sample container.
2. Keep glassware, hexane, distilled water, and sample below 23°C.

TABLE 3

Effect of Temperature and Exposure on PCB Spike Recovery

Conditions ¹	Recovery by Extraction, %	Recovery from Fibers, %	Total Recovery, %
Closed, cool (A)	88.4	11.0	99.4
Open, cool (B)	87.0	13.4	100.4
Closed, warm (C)	76.9	15.2	92.1
Open, warm (D)	73.4	12.2	85.6

¹One percent hardwood suspension, 57.1 µg/l. Aroclor 1242, 5 minutes stirring with magnetic stirrer. Warm = 30-32°C. Cool = 22-23°C.

3. Pour hexane into separatory funnel before introducing sample.
4. Maintain layer of hexane on top of aqueous phase.
5. Filter fibers as soon as possible.
6. Avoid pulling air through fibers during filtration.
7. Cook fibers in alcoholic KOH promptly.

Steps 1 through 4 should be of value in isolating PCB's from any aqueous sample. The layer of hexane seals the air-water interface from which volatilization can occur. Steps 5 through 7 are critical if the sample contains suspended fibers from which PCB must be extracted separately. Over half of the Aroclor 1242 has been lost from fibers when they were permitted to air dry before being placed in alcoholic KOH.

SAMPLE STABILITY DURING STORAGE

The need for special extraction procedures to remove PCB's from cellulose fibers suggests that the PCB's are sorbed onto the fibers. Table 2 shows less Aroclor 1242 volatilization from the softwood suspension than from the aqueous solution without fibers. Perhaps sorption of the PCB onto the fibers protected the PCB against volatilization. Sorption would also explain the improved stability of Aroclor 1242 during storage of fiber-water suspensions, compared with aqueous solutions, demonstrated in Figure 1. In that study, the spiking level was 86 µg/l. Aroclor 1242 in river water, and the suspensions contained 1% softwood fibers. Samples were stored in daylight at ambient temperature. Half of the samples contained formaldehyde at 15 ml/l. In a separate investigation, no stability

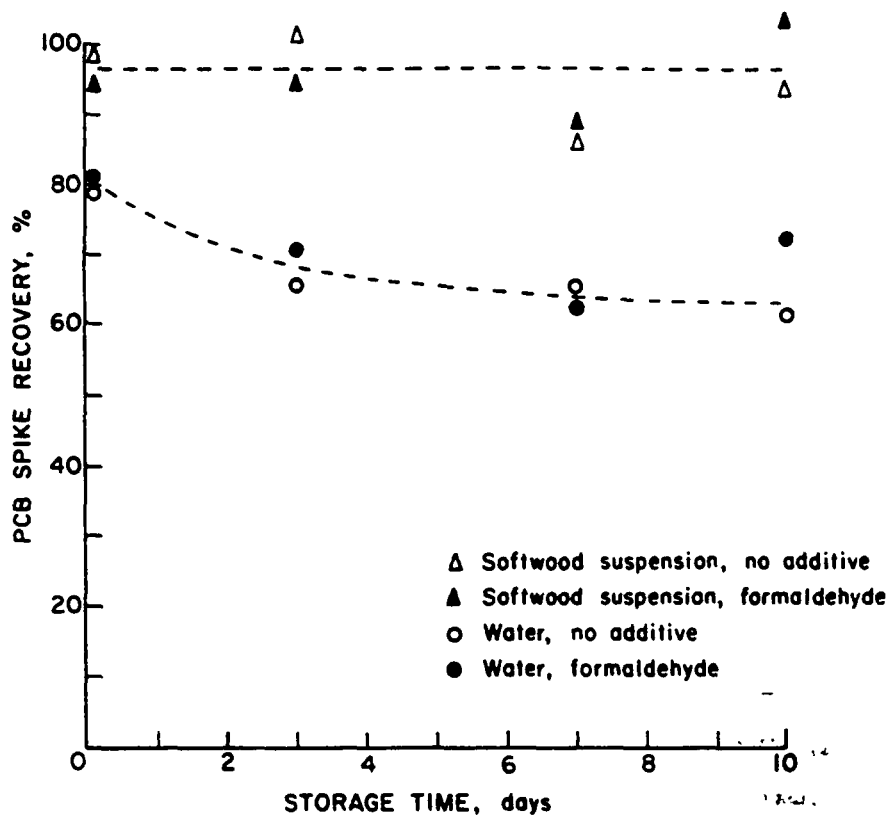


FIG. 1

Stability During Storage of Water and Fiber Suspensions Containing Aroclor 1242.

differences were observed between Aroclor 1242 solutions stored for 10 days in daylight vs. in the dark.

This study did not confirm the finding of Bellar and Lichtenberg that formaldehyde was an effective preservative for PCB's.⁷ However, an indirect benefit from adding formaldehyde to industrial effluents and fiber suspensions has been experienced: Formaldehyde

inhibits decomposition of non-PCB organics which degrade to liberate sulfur, a common interference on PCB gas chromatograms.

REMOVAL OF INTERFERING PEAKS FROM CHROMATOGRAMS

Perchlorination

Extracts from paper mill effluents should always be cleaned up on a Florisil column prior to gas chromatography. However, it does not remove all interferences. It was hoped, therefore, that the PCB's in paper mill effluents could be perchlorinated to decachlorobiphenyl (DCB), whose long retention time would move it well away from interfering peaks.

The perchlorination procedure used was essentially the method of Huckins, *et al.*⁶, modified in order to promote complete perchlorination with minimized volatilization loss of Aroclor 1242. The principal modification consisted of concentrating the extract containing the suspected PCB at room temperature in a culture tube by directing a stream of nitrogen at the top of the tube.

Perchlorination was attempted on authentic effluents from recycling mills as well as on distilled water containing Aroclor 1242 plus other suspected high-boiling components of recycled carbonless copy paper (alkyl biphenyls and alkyl naphthalenes). Reaction mixtures consistently charred, and low DCB yields were obtained on these spiked samples. Aroclor 1242 is thought to occur in paper mill effluents because of the recycling of carbonless copy paper made prior to mid-1971. If pre-1971 carbonless copy paper (with

PCB's) is present in a mill's raw material, newer carbonless paper (with alkyl biphenyls, alkyl naphthalenes, or other high-boilers, but not PCB's) is probably also present. Consequently, a mill effluent containing PCB's would quite likely also contain the alkyl biphenyls, alkyl naphthalenes, or other high-boiling compounds. Because these non-PCB components of modern carbonless copy paper reduce the DCB yield, perchlorination of paper mill effluents is apt to give incorrect estimates of the effluents' PCB contents.

Alkyl biphenyls and naphthalenes were also subjected to perchlorination in the absence of PCB. Reaction products were analyzed by FID gas chromatography using temperature programming to improve peak resolution. All samples yielded a peak with the same retention time as DCB. Thus, effluent analysis using perchlorination might incorrectly identify these originally nonchlorinated compounds as PCB's. Consequently, perchlorination is not recommended for determining or confirming PCB's in paper mill effluents.

Mercury and Chromium Trioxide

Interferences due to sulfur may be removed with mercury¹ or, as an alternative, chromium trioxide oxidation⁹ followed by a second Florisil cleanup, as shown in Fig. 2. Recoveries of Aroclor 1242 spikes carried through the chromium trioxide treatment have been approximately 90%. Gentle concentration of the sample extract in the presence of acetic acid is required to prevent loss of the more volatile Aroclor 1242 constituents.

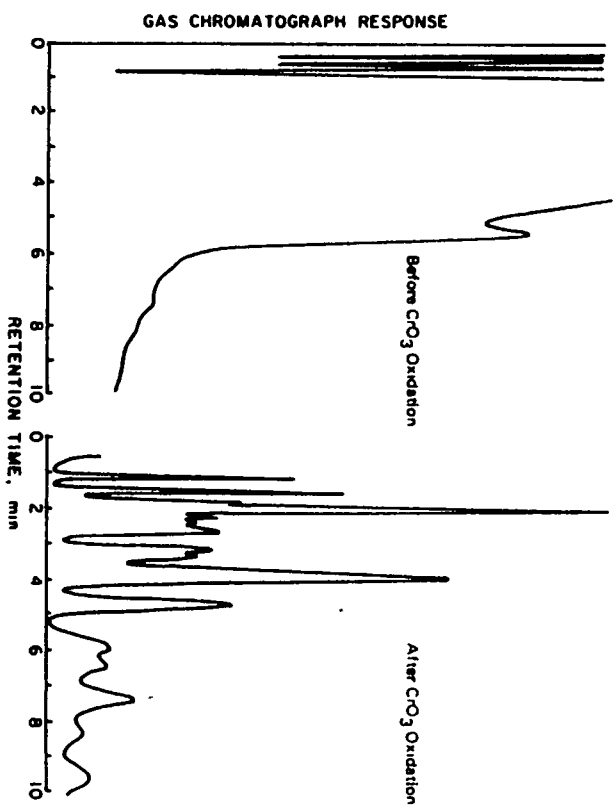


FIG. 2

Pulp Mill Effluent Spiked with Aroclor 1242.

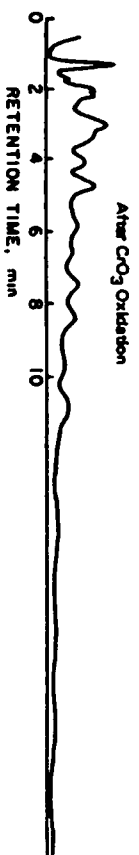
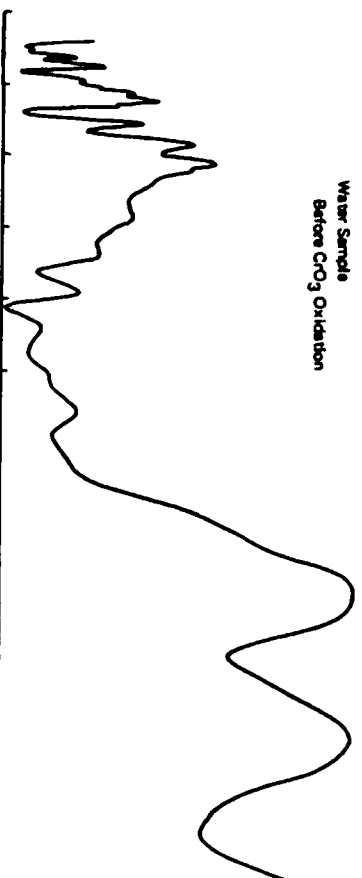


FIG. 3

Effect of Chromium Trioxide Oxidation on Water Sample Containing Interferences.

Alkyl naphthalenes, a possible component of newer carbonless copy paper, were removed by the chromium trioxide oxidation, but alkyl biphenyls were not affected. Figure 3 shows the result of using the chromium trioxide oxidation on an extract whose original chromatogram contained large unidentified interferences.

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